AN INVESTIGATION OF THE METHOD

OF

MEASURING IONIC MOBILITIES BY OBSERVATIONS ON

THE SELF-REPULSION OF IONS.

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Introduction.

In view of the large amount of discussion, which has centered around the measurement of ionic mobilities, of the complexity of the results obtained, and the possible uncertainty as to how far these results may be attributable to measurement, rather than to the properties of the ions themselves, it is desirable that the problem should be attacked from standpoints as varied as possible. The self-repulsion method is so different in its general properties from those usually employed, that it seems desirable to consider its possibilities in this respect, and the purpose of the present investigation is to subject this method to a critical examination from ~~the~~ both the experimental and theoretical side. In addition, measurements have been made of the mobilities of the positive and negative ions of air, carbon dioxide, oxygen, nitrogen, acetylene, and nitrous oxide at atmospheric pressure and room temperature.

On account of its bearing upon the general situation, a brief account of previous results obtained on the measurements of ionic mobilities is herewith appropriate.

Previous results on ionic mobilities.

In 1897 Rutherford[1] made the first measurement of specific

1. Rutherford, Phil. Mag. (5) 44 p 429 - 1897.

velocity of gaseous ions. Zeleny[1] was the first to discover the difference between the velocity of the positive and negative ions. Soon after this, Townsend[2], Wellisch[3], and Frank and Pohl[4] made measurements of mobilities of ions in different gases and vapours. It was shown in general that the mobilities were lower in the heavier gases. The investigation of the variation of mobilities with pressure was carried on by ~~Rutherford~~[5], Lattey[6], Kovarik[7], Todd[8], Townsend[9], and Frank[10]. It was found that the mobility varied inversely as the pressure and directly as the field. It was found, however, that for pressures below 10 cm., the mobility of the negative ion increased more rapidly than could be accounted for by the law $v=kx/p$ (where v is the mobility, x the electric field, p the pressure, and k a constant of proportionality). No such phenomena were observed in the case of the positive ion.

To explain this abnormal increase in the velocity of the negative ion with reduced pressures, two theories were advanced. One of these was the so-called "Cluster" theory. The advocates of this theory claimed that the negative ion was made up of a group of molecules clustered about an electron. As the pressure of the gas was reduced, the cluster was supposed to release some of its atoms or molecules, thus causing the cluster to have a

1.J.Zeleny-Phil.Trans.A 195,p.93,1900.
2.J.S.Townsend-Phil.Mag.(5) 45,p.135,1898.
3.Wellisch-Phil.Trans.A 209,p.249, 1909.
4.Frank and Pohl-Deutsch Phys.Gesellsch.Verh.9,page 195,1907.
5.J.Frank-Deutsch Phys.Gesellsch.Verh.12,p.291,1910, and Verh.12, p.613,1910.
5.Rutherford-
6.R.F.Lattey-Proc.Roy.Soc.A 84,1910.
7.A.Kovarik-Phys.Rev.30,p.415,1910.
8.Todd-Phil.Mag.S 6,Vol.22,p.791,1911,and Phil.Mag.June 1913.
9.Townsend-Proc.Roy.Soc.A85,1911.
10.J.Frank-Ann.Der Physik 22,p972, 1906.

greater mobility. The second theory was the "free electron" theory. Its supporters contended that the abnormal increase in mobility at low pressures was caused by the presence in the gas of a relatively large number of free electrons. They argued that for some reason the conditions for an electron, which must be produced when an atom is ionized, to form an ion were less favorable at lower pressures.

Of course, the task before the advocators of the "cluster" theory was to find conditions under which the cluster changed size, this fact being manifested by an abrupt change in the mobility; or to prove that in a gas there were groups of molecules, each group having a characteristic mobility. Nolan and McLelland[1], Moore[2], and Haines[3], are some of the more recent upholders of this theory. Noland and McLelland, and Haines claimed to have found such groups. Kia-Lok Yen[4], repeated Haines' work, but was unable to find these groups. Blackwood[5] with a method, having a resolving power 18 times higher than the method of Nolan and McLelland was also unable to distinguish groups of ions, having different mobilities.

The supporters of the "free electron" theory were more sucdessful than those of the "cluster" theory. Wellisch[6] showed that there were two types of negative carriers, the free electron and the ion. He gave evidence to show that a free electron remains a free electron and an ion remains an ion throughout a change of

1.Nolan and McLelland-Proc.Roy.Irish Acad.Vol.33,p.9-p.24, 1916.
Nolan-Proc.Roy.Soc.A Vol.94, 1917.
2.Moore-Phys.Rev.1912.
3.Haines-Phil.Mag.S6,Vol.30,1915,and Vol.31, 1916.
4.Kia-Lok Yen-Phys.Rev.1918, p.337.
5.Blackwood-Phys.Rev.1920. August
6.Wellisch-Am.Journal Science,May 1915.

pressure from one atmosphere to 15 mm. The ratio of the number of electrons to the number of ions increases with decrease in pressure.

Loeb[1] went further to disprove the "cluster theory" by subjecting the ions to such intense electric fields that the ions would acquire energy almost sufficient to ionize an atom. Loeb was of the opinion that an ion having sufficient energy to ionize ought certainly to have energy enough to break down a cluster. The criterion for determining such a "breakdown" would be a sudden definite increase in the mobility. No such increase was found. Kia-Lok Yen repeated Loeb's work, using higher fields and still found no indications of the breaking down of the ion.

By all these experiments then, the "free electron" theory may be said to have been established. The main problem then confronting investigators was the question of what conditions are necessary for an electron to form an ion.

Wellisch[2] advanced the theory that an electron must have more than a certain minimum of energy where it collides with an atom or molecule if it is to form an ion. He supposed that the electron has its maximum energy when it leaves the parent atom, and that if the electron does not suffer collision within a certain radius of this atom, it will remain an electron.

THomson[3] held a different view. He held that one out of every n collisions of an electron with an atom or molecule will result in the formation of an ion. n varies with different gases. This law does not limit the conditions for formation of ions to energy considerations.

1. Loeb - Phys.Rv. Vol.8, p633, Dec.1916.
2. Wellisch - Am.Jour.Sc, Vol.39, 1915.
3. J.J.Thomson, Conduction of Elec. theough Gases.

Loeb[1] recently has carried out an investigation which goes far toward establishing Thomson's theory.

Of course during the time that the structure of the negative ion was of greatest interest, other work in mobilities was carried out also. The effects of temperature, moisture, impurities and age on the mobilities of gaseous ions were investigated.

Also while the discussion of the size and change of size of the negative ion was taking place, it seemed to be taken for granted that the positive ion remained unchanged. The results of some work which Professor Erikson is now doing seem to show that the mobility of the negative ion is independent of its age, whereas that of the positive ion decreases as the ion becomes older.

In performing all of these investigations of ionic mobilities various methods have been used. Only one or two methods, however, have found favor in recent years. Kovarik, Wellisch, Loeb, Haines, and Kia-Lok Yen have used the Rutherford alternating field method in which the distance an ion travels in a known time under a known field is measured. Zeleny's method in which the field necessary to take ions over a certain path in a known time is measured, was used by Blackwood. A method somewhat similar to the Zeleny method has recently been used by Professor Erikson.

The Self Repulsion Method.

The method whose possibilities are to be studied in this investigation, is theoretically the same as that used by Townsend for measuring the velocity of very slowly moving ions. We shall see later why it is necessary that a different apparatus be used for measuring higher mobilities.

1. Loeb, Phys.Rv. Feb. 1921.

Townsend[1] realized these conditions experimentally by blowing uniformly ionized gas into a conducting tube which was earthed and connected to an electrometer. The tube was then insulated and after a time t the charged gas was blown out. The electrometer then measured the charge remaining in the gas when it was blown out. Although this method may have succeeded for measuring the mobility of slowly moving ions, there are several reasons why it could not be used for more rapidly moving ions. First of all, it is desirable to have a high density on account of diffusion, but if Townsend's method were used, a high initial density would result in a great loss of charge while the ionized gas ~~were~~ was being blown into the cylinder. Secondly, it would be difficult to know the exact time at which the gas was driven out of the chamber. For instance, in the present experiment it was necessary to take into account times of the order of .01 sec. Then while the charge is being blown out of the cylinder, charge would be lost to the walls of the apparatus. A different amount would be lost at each reading for different time intervals, since the amount lost depends upon the density. A calculation of this error would be very difficult since the error depends upon the mobility which is being measured and the time during which the ions ~~were~~ are being driven out, and the density which is varying during this time.

Let us consider another method for making the same type of measurements. The essential features of this method will be made clear by a reference to figure 1.

1. Townsend, Phil.Mag. (5)45 p 135. 1898.

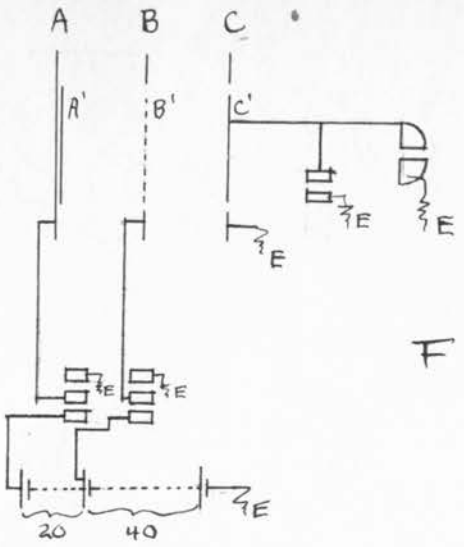


Fig. I.

A, B and C are parallel conducting plates. B consists of a grid B' surrounded by a wide metal frame; on A directly opposite the grid B' on the side of A toward B', there is a polonium plate A' and C consists of a plate C' equal in area to B' and A', insulated from a guard ring around it and connected to an electrometer.

Let C be at zero potential, B at plus 40 volts and A at plus 60 volts. The positive ions generated in the space between A and B will be driven toward B and some of them will pass through the grid to the plate C, In fact an ionic current of practically uniform density will pass from the grid to the plate C. (The extent to which the current density is not uniform will be discussed later.) Now suppose that A and B are simultaneously earthed. The space between the grid and the plate C' will be filled with positive ions of uniform density. Suppose that the ions are allowed to move about at will for a time t; at the end of this time, insulate plate C' and raise plate B again to a potential of plus 40 volts, plate B remaining at zero potential. The positive ions then between B' and C' will be drawn to C and the charge given up by them to plate C', ~~where it~~ may be measured. During this operation no additional ions will pass through the grid, since the positive ions between A and B will now be drawn to A

and the negative ions in the whole system will be driven to B. This arrangement then makes possible the investigation of the charge contained in the volume between B' and C' at any time.

There is another factor pointed out by Dr.Swann which must be considered whenever ions are cleared out of a space, and their charge measured. Owing to the fact that the plate C is earthed while the ions are being brought into the region between B and C, C will have an induced charge of sign opposite to the charge between the plates, so that when C' is insulated and charges are drawn to it, it will be the algebraic sum of the true charge and the induced charge which is being measured. In order to measure the true charge, the induced charge must be measured and added to this algebraic sum. The process of measuring the latter shall be referred to as Case I, the process of measuring the induced charge shall be called Case II. In Case II the operations are performed exactly as they are in Case I up to the point where the potential is put on B to drive the ions remaining to C. In Case II, the potential put on at this time is opposite in sign to that put on at the corresponding time in Case I. Thus the ions are drawn to B, leaving only the induced charge on C' to be measured. The sum of the charges measured in Case I and Case II for corresponding time intervals, gives the true charge which it is desired to measure. Thus by a method, such as outlined above, the fundamental conditions of the experiment may be fulfilled.

Apparatus.

The apparatus actually used in the experiment is repre-

sented in detail in Figure 2. The plates A, B and C are made of brass, and are 16cms.square. A polonium plate A' 8cms.square is soldered to the middle of plate A, on the side toward B. Directly opposite to A' in B is a grid B' also 8cms.square. This grid consists of horizontal strips of brass about 3mm.wide with spaces 3mm. wide between the strips. Directly opposite the grid, in C is an 8cm.plate C' insulated from the rest of the plate C, this part serving as a guard ring.

Plate B is fastened to and insulated from plate A by means of four hard rubber cylinders L,N, while plate A is supported by and insulated from the iron stand X. Plate C' and the guard ring are both fastened to and insulated from the iron support Y. Plate B is placed 4 cms. from either plate A or plate C. The supports X and Y rest on an iron track which rests on a pump stand P. The plates are surrounded by a tin shield T, which is in turn surrounded by a bell jar J, which also rests on the pump stand. There is a rubber packing between it and the stand. By means of the frame Fr and Screw Sc, the bell jar is clamped down tightly to the pump stand. The brass cup η , which is covered with a brass screen, contains P_2O_5.

Electrical connections to the plates are made through four wires a, b, c, d, which pass through a sulphur plug S in the pump stand. Wire a is connected to plate A, wire b to B, wire c to C' and d to the guard ring.

The potentials used were obtained from three trays of storage batteries F, each tray having a voltage of 80 volts. These batteries were connected in series and the terminals connected to a double pole double throw switch G. One pole of the switch was connected through keys 1 and 4 in parallel to one end of a series R of 20 resistance coils, of 1000 ohms each. The other pole of the switch was connected directly to the other terminal of the resistance coils. Of course by means of the double pole, double throw switch the potential at the ends of the resistance coils could be reversed.

Wire a is connected to the middle part of key 2. Wire b is connected permanently to coil 14 of the series of resistance coils, and also to one terminal of a battery (H) of 20 volts whose other terminals is connected to the lower part of Key 2. Wire d is earthed permanently. Wire c is connected to the upper part of Key 3, to one pair of quadrants of the electrometer Q and to the inner cylinder of a small variable condenser D. The outside of the condenser is connected to coil 19 of the resistances R. The electromter needle is connected to coil 2. Coil 12 is connected to a variable contact on the resistance K whose terminals are maintained, one at zero potential, the other at about 3 volts. A voltmeter V measures the difference of potential between the earthed end of the resistance and the contact point. Except when a reading is being taken the contact remains at the earthed end of the resistance.

Keys (1) (2) (3) (4) are operated respectively by four electromagnets (1′) (2′) (3′) (4′). The circuits through these electromagnets and cells I are completed when the brush U mounted on a pendulum Pm passes over the contact plates 1", 2", 3",

4". The contact plates 3" and 4" may be removed from the track of the pendulum, and their function may be performed by two Keys 5 and 6 which are operated by hand. In series with electromagnates 1' and 4' are electromagnates controlling ~~the~~ a stylus of a chronograph Ch, while another stylus is operated by an electromagnet the circuit through which is completed once every second.

Procedure.

First of all the potential on the outside of the variable condenser D was chosen so that by an adjustment of the capacity of the condenser there was no deflection - or a very small deflection of the electrometer needle ~~was~~ produced when all the potentials were thrown on the system, that is when Key 1 or 4 was closed, 3 open and plate A earthed. By means of this arrangement, which was devised by Dr. Swann it is seen that any fluctuations in the potentials used, produces ultimately no effect on the insulated system. Where there is charge of one sign induced on the insulated system on account of fluctuation of potentials, there will be induced on it also an equal charge of the opposite sign. This is obviously a great advantage. Still another advantage will be discussed later.

In the condition which we may call the "dormant" condition of the apparatus, part α of Key 2 is closed thus maintaining a difference of potential of 20 volts between plate A and plate B. Key (1) is closed thus placing a potential of about 40 volts on plate B, 100 volts on the electrometer needle and about 80 volts on the condenser D. Key 3 is closed, thus earthing the quadrant connected to plate C'. Key 4 is open.

Three or four seconds before a reading is to be taken, the chronograph is started.- Then the contact pendulum is released. As the brush passes over contact 1", Key 1 is opened, thus earthing plate B, the outside of the condenser and the electrometer needle. As the brush passes over contact 2", part α of Key 2 is opened, part β closed, thus earthing plate A. These two operations occur almost simultaneously the time interval between them being about 1/50 second. As the brush passes over contact 3", Key 3 is opened, insulating plate c' and the quadrant. The brush in passing over contact 4', causes Key 4 to be closed, thus replacing the potentials on condenser D electrometer needle and plate B (the interval between operation of 3 and 4 is small). The chronograph is then stopped.

As the electrometer needle begins to deflect, the contact on resistance K is moved so that the needle is brought back to its zero position and kept there until the end of two minutes from the time when the pendulum was released. The voltmeter is then read. The contact is moved back to the earthed point and the apparatus put in the "dormant" condition again. The advantages of this arrangement are: Keeping the insulated system at zero potential, and as we shall see, ease in calibration.

By repeating this whole process for various intervals of time between the operation of Key 2 and of Key 3, a set of readings for Case I is obtained.

For obtaining a set of readings for case II the two wires carrying potentials to the double pole double throw switch G are reversed. The switch G itself is also reversed, thus leaving the potentials the same as in Case I. The operations for Case II

are exactly the same as for Case I until after the brush has passed contact 2". Then the pendulum strikes the lever Lv which is rigidly connected to the handle of the switch G, reversing the sign of the potentials leaving G. Now when key 4 is closed the potentials applied to the system will all be of opposite sign to those applied at corresponding times in Case I. The rest of the operations then are performed as in case I, except that in order to bring the needle back to the zero position, the potentials at the ends of the resistance K must be reversed, keeping the same end of the resistance earthed, however. Before taking a second reading, of course the system must be again put into the "dormant" condition which it is to be remembered is the same as the dormant state for Case I. Variation of charge with time is obtained for Case II as for Case I.

Let us note here another advantage of the compensation method described on page 12. This arrangement makes it possible to insulate plate C' before putting the potential on B to drive the ions to C, since the induction effect is nil or a small measurable quantity. Without this compensation device, the plate C' could not have been insulated until after the field had been put on. In this case all the ions drawn to the plate C' in the interval of time between the putting on of the field and the opening of the electrometer key would be lost.

To obtain the "balance" for either Case I or Case II, the apparatus is arranged as in the "dormant" state, except that the B part of Key 2 is closed thus earthing the plate A so that no ions are being driven into theregion between B and C. The rest of the process is the same as in the case of a regular reading. By this means all effects (including effects due to natural ionization)

are taken into account, except the effect due to the ions, that is the effect we wish to measure. The difference then between the "balance" and the actual reading, gives the values desired.

The apparatus is calibrated by connecting a Gerdien condenser to wire C, putting a potential of .040 volts on the outside of the condenser, insulating plate C', wire c and inner cylinder of the variable condenser D, changing the capacity of the condenser by 105×10^{-6} micro-farads, and bringing the electrometer needle back to zero in the usual way and taking the voltmeter reading. Then the operation is repeated putting a potential of .020 volts on the condenser, and altering its capacity by the same amount as in the previous case, then bringing the needle to zero position and noting again the reading of the voltmeter.

If V = potential put on condenser in the first case.

V' = " " " " " " second case.

D = deflection in the first case.

D' = " " " second case.

dc = change in capacity of the condenser in either case, the relation

$$(V - V')dc = C(D - D')$$

gives C the charge which must be put on the system in order to have to raise contact point on K to a potential of .01 volt in order to bring the electrometer needle to the zero position. Thus the charge on the insulated system can be deduced from the voltmeter readings. A calibration of the apparatus was made for every set of readings taken.

When a gas was to be introduced into the bell jar, the bell jar and the connections from it to the gas container were evacuated to a pressure of five centimeters and the gas was allowed to flow into the jar through a cylinder of KOH and another of cotton wool. The jar was always evacuated and refilled with the gas from four to six times before allowing the gas to remain. Any moisture left in the gas would be removed by the $P_2 O_5$ in the bell jar.

Special efforts were made to obtain as large density of ions as possible. A strong polonium plate 8 cm. square was prepared. With this plate as a source of ionization, the next problem was to get as many ions as possible into the region between B and C. Experiments were performed to find out what fields between A and B, and B and C would give the largest charge density. It was found that about 20 volts between A and B, and 40 volts between B and C gave the most satisfactory results. Various types of grids were also tried; grids made of heavy wire, with large meshes; grids made of fine wire with small meshes; grids made of fine wire with large meshes. Usually the grids that permitted a large charge density, also allowed ions to enter the region between B and C where there was no field driving them in. The grid which gave the largest density without permitting ions to come through when there was no field driving them through, was the grid used in the experiment and described on page 10.

Discussion of experimentally measured values of charge density.

As mentioned above the value of the potential difference between B and C which gave the largest charge densities, was 40 volts. Then if the mobility is of the order of one centimeter per second per volt per centimeter, it will take an ion about .4 second to cross the space between B and C. While the ions are being driven in the direction of the field they will also be spreading out in all directions on account of the self repulsion just as they would as if there were no external field. The ionic density will therefore be greater near B and than near C. Let us make a calculation to find the ratio of these two ionic densities. Let us assume that $\rho_0 = 4 \times 10^{-4}$

Then $\frac{1}{\rho} = \frac{1}{\rho_0} + 4\pi kt \times 300$ when ρ is in e.s.u.

$= 2500 + 4\pi \times 1 \times 4 \times 300$

$= 4000$ approximately

$$\frac{\frac{1}{\rho}}{\frac{1}{\rho_0}} = \frac{\rho_0}{\rho} = 1.6$$

Let us see what difference in the calculation of the mobility will be made by this departure from uniform density. The experimentally measured value of charge density $\bar{\rho}$ is Q/V where Q is the total charge and V is the volume between B' and C'. The true ρ in any volume element is $\rho = \bar{\rho} + \epsilon$ where $\int \epsilon \, dV = 0$

Whatever the nature of the distribution of charge, the following relation holds $-\frac{1}{K}\frac{dQ}{dt} = \iint R_n \rho \, ds = \iint R_n (\bar{\rho} + \epsilon) \, ds$

$$= \bar{\rho} \iint R_n ds + \iint R_n \epsilon \, ds$$

where R_n is the electric force normal to the surface bounding the

charge Q. Using Gauss' theorem this expression becomes

$$-\frac{1}{k}\frac{dQ}{dt} = \bar{\rho}\,4\pi Q + \iint R_m \epsilon\, ds$$

or $$-\frac{1}{k}\frac{dQ}{dt} = 4\pi\frac{Q^2}{V} + \iint R_m \epsilon\, ds$$

Now if $\iint R_m \epsilon\, ds$ can be shown to be negligible, k may be calculated from the expression given above. Dividing this expression by V it becomes $-\frac{1}{k}\frac{d\bar{\rho}}{dt} = 4\pi\bar{\rho}^2$ which is of the same form as the expression for k in terms of uniform charge density.

We must now try to show that $\iint R_m \epsilon\, ds$ is negligible. From the calculation on page 17 we see that the maximum ratio of ϵ to $\bar{\rho}$ is one fourth of .6/1.3 because 1/2 of .6 is the maximum deviation from the mean value (which corresponds to 1.3) and 1/4 of .6/1.3 is the average ϵ. This amounts to about 9%. The ratio is really not as large as this because although we cannot say that $\int \epsilon\, ds = 0$, ϵ is of opposite sign near the plate B and near the plate C. If ρ were a linear function of kt, ϵ would be zero. Such is actually not the case but the ϵ's will tend to cancel out so that it would seem safe to say that on this account $\int \epsilon\, ds$ would become a small fraction of 9% of ρ.

There is another way of arriving at the same conclusion. Suppose $\iint R_m \epsilon\, ds$ were not negligible. The linearity of the relation $\frac{1}{\bar{\rho}} - \frac{1}{\bar{\rho}_0} = 4\pi k t$ would be destroyed unless both R and ϵ were proportional to Q. R is of course proportional to Q but ϵ cannot be since the portions of greater density lose charge more rapidly than the less dense portions, and ϵ will decrease more rapidly than will the average value of Q. If this is true, and the linearity of the relation between $\frac{1}{\bar{\rho}}$ and t is not destroyed, as we shall see that it is not, we

may conclude that $\frac{1}{\rho} - \frac{1}{\rho_0} = 4\pi K t$ gives the true value of k.

Another possible source of error lies in the fact that in measuring the charge, the electrometer quadrant is insulated about .02 sec. before the field is put on to draw the ions to C. During this .02 second, charge is lost from the volume between B' and C'. Some of the charge lost goes to the plate C' and makes the charge measured too large. Let us use the expression $\Delta\rho = \rho^2 4\pi K \Delta t$ in calculating the percent of charge lost in this time.

$$\frac{\Delta\rho}{\rho} = 4 \times 10^{-4} \times 4\pi \times .02 \times 300 = .03$$

Thus the total percent of charge lost in this time is only 3% so that the part of this which goes to the plate C' must surely be less than 1%, and is therefore negligible.

As was mentioned on page 16, differences of potential of 20 and 40 volts between A and B and B and C were the best combination of voltages for driving the ions into the space between B and C. This being the case, the simplest arrangement for finally drawing the ions to C was to replace the potential of 40 volts on plate B. This was done as described on page 13. Now if the mobility of the ions is of the order of 1 cm. per sec. per volt per cm. and the potential gradient is 10 volts, it will take about .4 sec for an ion to pass from plate B to plate C. During this time the charge contained in the volume between B' and C' would decrease appreciably. Picture what happens in this region when the potential is put on B. All of the ions are being driven toward C at the same time they are spreading out in all directions due to self repulsion. Those escaping from the volume between B' and C' in a direction perpendicular to direction

Theory.

Suppose that we have a charge distribution of density ρ . Suppose the velocity of the charge in the x direction is u, in the y direction v, and in the z direction w. Then we have from the equation of continuity

$$-\frac{d\rho}{dt} = \frac{\partial \rho u}{\partial x} + \frac{\partial \rho u}{\partial y} + \frac{\partial \rho v}{\partial z}$$

if ρ be uniform and since $u = -k\frac{\partial V}{\partial x}$, $v = -k\frac{\partial V}{\partial y}$, $w = -k\frac{\partial V}{\partial z}$ from the definition of mobility k, where V is the potential

$$\frac{1}{\rho}\frac{d\rho}{dt} = +k\left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2}\right)$$

but from Poisson's equation

$$-\nabla^2 V = 4\pi\rho$$

so that $\frac{1}{\rho}\frac{d\rho}{dt} = -4\pi k$ which when integrated becomes

$$\frac{1}{\rho} - \frac{1}{\rho_0} = 4\pi k t$$

and

$$k = \frac{\rho_0 - \rho}{\rho\rho_0 4\pi t}$$

Thus if measurements of density of different times be made, one has all the data necessary for measuring k since k is a function of density and time only, and is independent of applied field and distances traveled by the ions.

In order to make use of the relation $k = \frac{\rho_0 - \rho}{\rho_0 \rho 4\pi t}$ in measuring the mobility k , the conditions sought for expermentally are (1) uniformity of concentration of ions (2) in a chamber where ions could move about for any desired length of time t in the absence of any electric field other than that due to their own charges, and (3) the possibility of measuring the density of ions at any desired time.

of the external field are lost. Upon careful thought it became apparent that it was extremely difficult to make an accurage calculation of the amount so lost. A correction for this loss however must be made. It was done in the following way.

A potential of 800 volts was put on B to drive the ions to C. This potential was entirely independent of the old system. It was put on immediately after key 3 was opened. After 5 seconds it was taken off and key 4 closed, leaving conditions the same as in the old method of proceedure, for any inductive effects caused by the 800 volts would be annulled when this potential was removed. By this method ions would be drawn across the space between B and C in less than .02 second during which time the loss in charge would be inappreciable. A set of readings for Case I of the positive ion in air was obtained in this way. Several points on a corresponding curve of the old type were also obtained, so that the curves of old and new type could be correlated.

Case II was correctly determined in the first place since it only measures the charge on C' when it becomes insulated by the action of key 3, and is independent of the manner in which the ions between B and C go off to infinity.

Dr. Swann suggested a method whereby the correction to be applied to Case I for each ion could be determined from the curves. obtained experimentally for one ion - namely, the positive ion in air.

Suppose we have two systems A and B. Assume that the charge distribution is the same in both cases but that the ions in the two systems have different mobilities. Let the mobility in system

A be v, and that in system B, be V. Now let us divide the time into corresponding elements dt_1 , dt_2 - - - - and dT_1 , dT_2 - - - such that

$$v\,dt = V\,dT$$

In system A at dt an element of charge will have moved a length proportional to v dt. In system B, an element of charge will have moved a distance proportional to V dT. Now since v dt = V dT, corresponding elements of charge will be in corresponding positions at corresponding times. Thus the fields in the two systems are everywhere the same at corresponding times.

Let us go back to the actual experiment. Suppose that we have a certain concentration of positive ions in air in the space between B' and C' and we apply a field to drive these ions to C. A certain amount of charge becomes lost during the time it takes the ions to get across. We have now determined what this loss is. S uppose that we have the same concentration of ions in another gas. In the time it takes these ions to be drawn across, under the same external field, (this time being greater or less than in the case of positive ion in air, according as the mobility less than or greater than that of positive ion in air) the same amount of charge will be lost. Thus if the initial densities where the same, the amount lost the same, the part actually measured will be the same in both cases. It was on this basis that all the Case I curves were corrected. For instance take a point on the experimental curve for positive ion in nitrogen - find,the point on the positive ion in air curve, which corresponds to the same measured density, find what the corrected

density is from the experimentally corrected curve for positive ion in air, and that will be the proper density for the point on the positive ion in the nitrogen curve. The curves so obtained are given in the following pages.

Method of calculation.

The calculations of mobilities was made in one of several possible ways. Of course to get the true density corresponding to a given time the apparent densities given for that time in Cases I and II must be added. The reciprocals of these sums were plotted against corresponding times. Theoretically, if the mobility is a constant, this curve will be a straight line. The mobility is readily calculated from the slope of the line which is $4 \times 300 \times \pi \times k$. The $\frac{1}{\rho}, t$ curves are shown in the following pages.

Tables of Readings

C = constant by which voltmeter deflections must be multiplied to give charge density in e.s.u.

N = apparent charge density in Case I in e.s.u.

M = Apparent charge density in Case II in e.s.u.

t = time in seconds.

AIR

Positive Ion, Case I.

C = 9.65

Uncorrected		Corrected	
N	t	N	t
155.8	.11	171.0	.15
142.1	.17	106.0	.53
125.0	.24	139.0	.30
108.1	.35	72.3	.96
99.0	.49	59.8	1.30
73.5	.80	48.2	1.66
51.2	1.24	28.9	2.75
41.5	1.50	164.0	.21
143.5	3.21	115.8	.44
145.7	.15		
87.8	.52		

AIR

Positive ions

Date March 22.
Pressure 74.9 cm
Temp. 20° C

C = 9.45

Case I		Case II	
N	t	M	t
171.0	.10	79.8	.11
139.0	.25	69.0	.26
106.0	.48	57.7	.47
72.3	.91	49.1	.78
59.8	1.25	14.1	2.42
48.2	1.61	6.3	3.07
28.9	2.70	34.5	1.23
164.0	.16	36.8	1.14
115.8	.39	19.2	2.02

Negative ions

Date March 21.
Pressure 74.9 cm.
Temp. 21° C

Case I		Case II	
N	t	M	t
175.0	.10	86.0	.10
136.0	.26	73.5	.29
107.0	.47	58.6	.48
52.0	1.29	46.3	.75
38.4	1.96	36.1	1.14
34.4	2.34	31.5	1.34
117.0	.36	26.4	1.79
159.1	.17	19.2	2.48
69.4	.84	17.1	2.91
		8.5	4.61
		16.0	3.18

NITROGEN

Positive ions

Date March 11.
Pressure 73.4 cm.
Temp. 20° C

C = 8.60

Case I		Case II	
N	t	M	t
164.0	.15	94.6	.11
129.2	.25	80.8	.26
95.2	.47	66.2	.49
72.2	.73	57.8	.70
50.0	1.54	34.4	1.53
35.0	2.47	22.3	2.64
		16.3	3.35
		9.6	4.38
		38.7	1.35

Negative ions

Date March 9.
Pressure 73.6 cm.
Temp. 20° C.

Case I		Case II	
N	t	M	t
161.0	.11	75.8	.14
129.4	.25	68.5	.10
97.4	.47	58.8	.30
71.5	.76	52.4	.49
46.5	1.50	40.0	.82
26.9	2.46	38.3	.86
33.1	2.04	31.0	1.20
47.4	1.39	26.8	1.70
57.0	1.04	19.1	2.47
145.0	.20	15.7	2.90
113.0	.38	12.0	4.00

AIR (2nd set)

Positive ions

Date Feb. 2.
Pressure 73.6 cm.
Temp. 21° C

C = 8.25

Case I		Case II	
N	t	M	t
171.5	.15	89.5	.10
117.0	.50	74.6	.29
138.0	.25	62.2	.47
56.0	1.19	45.1	.89
46.6	1.76	35.0	1.41
36.8	2.46	16.8	3.16
76.5	.90	27.2	1.90
		22.6	2.55

Negative ions

Date Feb. 3.
Pressure 73.0 cm.
Temp. 21.5° C.

Case I		Case II	
N	t	M	t
134.9	.11	68.6	.10
120.7	.30	59.4	.25
86.0	.47	50.7	.47
49.5	1.00	34.0	.93
31.8	2.20	31.2	1.11
27.5	2.53	21.1	2.35
57.5	.93	16.3	3.56
38.3	1.53		

NITROGEN (2nd set)

Positive ions

Date March 3.
Pressure 75.8 cm.
Temp. 20° C

C = 8.81

Case I		Case II	
N	t	M	t
132.0	.11	68.8	.10
115.0	.18	60.4	.23
87.5	.47	51.1	.50
55.6	.85	39.0	.94
47.6	1.41	26.9	1.72
31.7	2.51	13.6	3.22
		18.2	2.75
		24.3	2.27

Negative ions

Date March 4.
Pressure 73.1 cm.
Temp. 20° C.

Case I		Case II	
N	t	M	t
145.0	.10	67.3	.10
114.0	.25	59.8	.27
85.8	.47	49.3	.46
55.3	1.08	38.8	.85
59.5	.94	26.1	1.67
48.4	1.31	19.0	2.66
40.0	1.84	24.2	1.89
44.3	1.66	69.6	.10

CARBON DIOXIDE

Positive ions

Date Feb. 11.
Pressure 73.9 cm.
Temp. 20° C.

C =

Case I		Case II	
N	t	M	t
158.6	.10	76.9	.10
137.4	.28	71.2	.27
109.7	.46	62.2	.45
71.0	1.06	52.2	.88
42.7	2.11	31.6	1.83
33.0	3.00	22.2	2.76
		16.0	3.60
		78.8	.10

Negative ions

Date Feb. 12.
Pressure 74.1 cm.
Temp. 21.5° C.

Case I		Case II	
N	t	M	t
146.9	.10	72.1	.10
122.6	.29	65.0	.27
103.6	.48	56.2	.48
68.4	.87	43.9	.86
53.2	1.44	27.3	1.81
40.0	2.14	19.9	2.24
29.2	3.13	14.9	3.42
		9.09	4.58
		33.1	1.40

NITROUS OXIDE

Positive ions

Date April 5.
Pressure 73.2 cm.
Temp. 21° C.

C = 9.64

Case I		Case II	
N	t	M	t
171.5	.10	89.6	.10
146.0	.25	80.0	.24
118.0	.45	66.6	.47
84.7	.91		
55.3	1.65		
33.3	2.77		

Negative ions.

April 9.
74.3 cm.
20° C.

Case I		Case II	
N	t	M	t
164.9	.10	74.1	.10
106.0	.47	50.2	.48
132.0	.26	61.7	.27
89.5	.64	40.5	.75
45.6	1.66	26.8	1.44
30.6	2.57	28.7	1.31
57.8	1.27	21.5	2.77
70.2	.89	38.5	.98
116.5	.37	68.9	.16
149.0	.17	56.5	.36

OXYGEN

Positive ions

Date March 16
Pressure 73.63cm.
Temp. 20°C

C = 9.54

Case I		Case II	
N	t	M	t
160.5	.26	101.5	.10
127.0	.47	90.0	.26
106.0	.66	75 .8	.47
51.0	1.49	59.6	.77
64.5	1.14	47.0	1.24
34.2	2.53	24.5	2.30
72.0	1.02	12.2	3.91
169.0	.225	36.7	1.61

Negative ions.

March 17
73.25cm.
21.5° C

Case I		Case II	
N	t	M	t
174.0	.14	87.8	.10
143.0	.25	75.2	.26
108.0	.46	58.1	.47
88.0	.64	51.2	.67
47.8	1.44	31.4	1.17
34.7	2.09	22.9	1.97
55.7	1.01	14.3	3.37
26.0	2.79	12.4	4.00
68.7	.85		
161.0	.20		

ACETYLENE

Positive ions

Date March 31
Pressure 74.9 cm.
Temp. 21° C

C = 9.00

Case I		Case II	
N	t	M	t
172.0	.25	97.02	.11
146.2	.46	187.1	.27
108.9	.71	71.9	.48
52.0	1.58	61.6	.71
35.0	2.46	30.3	2.03
28.5	2.82	27.3	2.35
72.3	1.08	35.4	1.73
43.1	2.03	52.5	1.00
		20.5	2.89
		16.6	3.68
		12.1	4.40

Negative ions

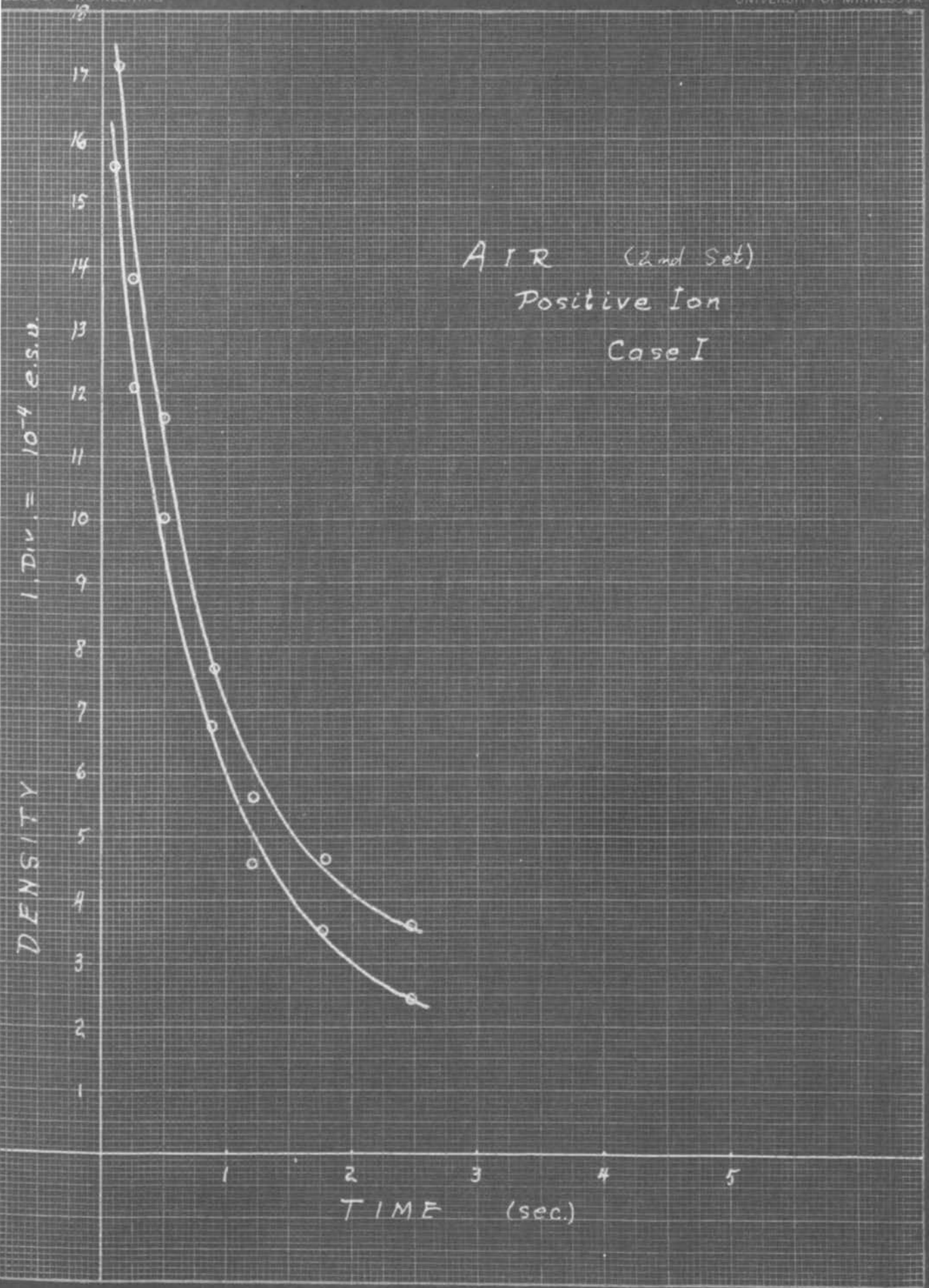
April 1
73.4 cm.
20°C

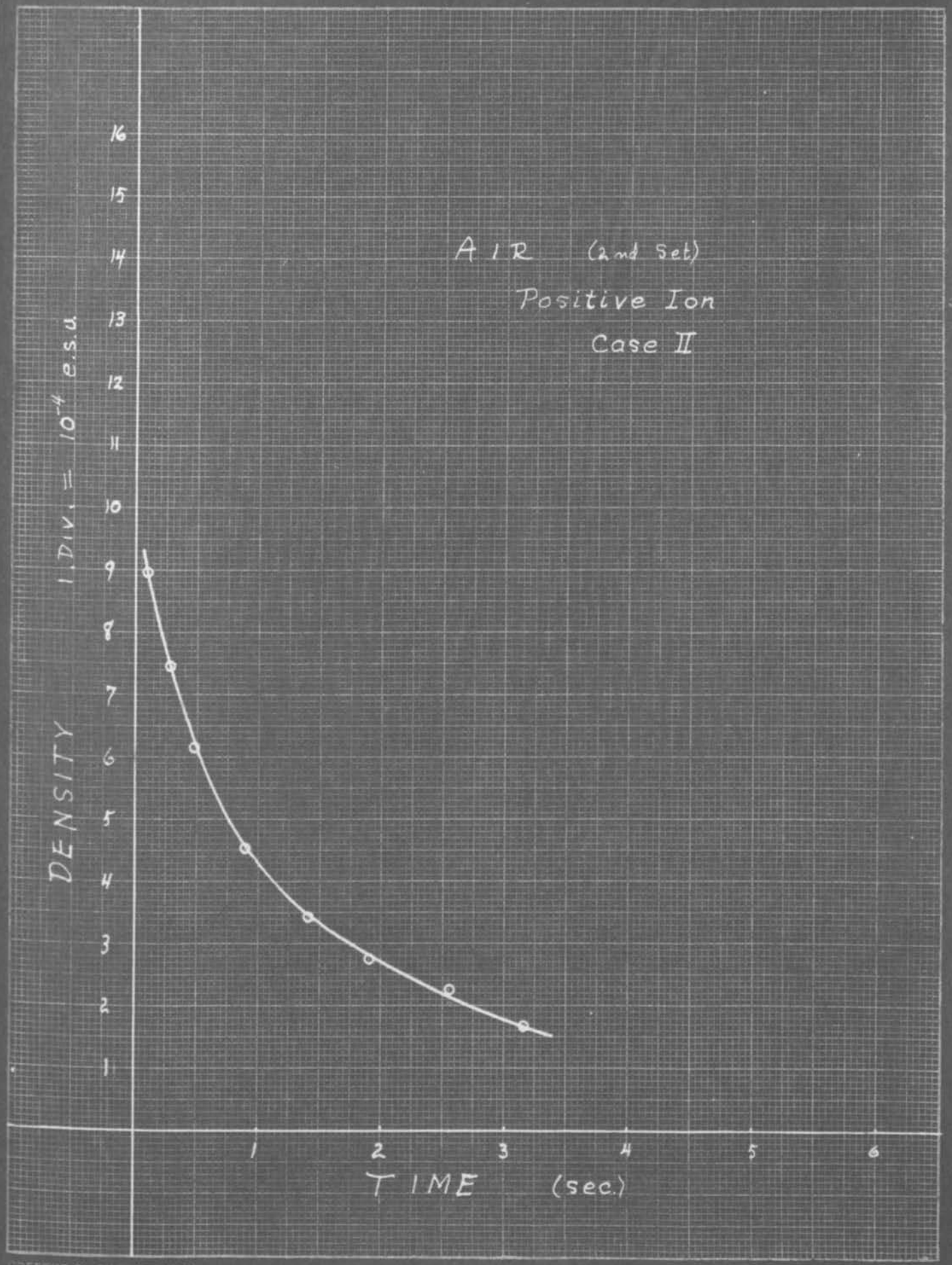
Case I		Case II	
N	t	M	t
168.0	.10	79.4	.12
135.0	.27	69.3	.26
103.0	.47	55.8	.47
74.2	.75	42.3	.88
57.6	1.13	14.9	2.59
36.0	1.85	9.0	3.57
		26.4	1.61
		80.1	.11

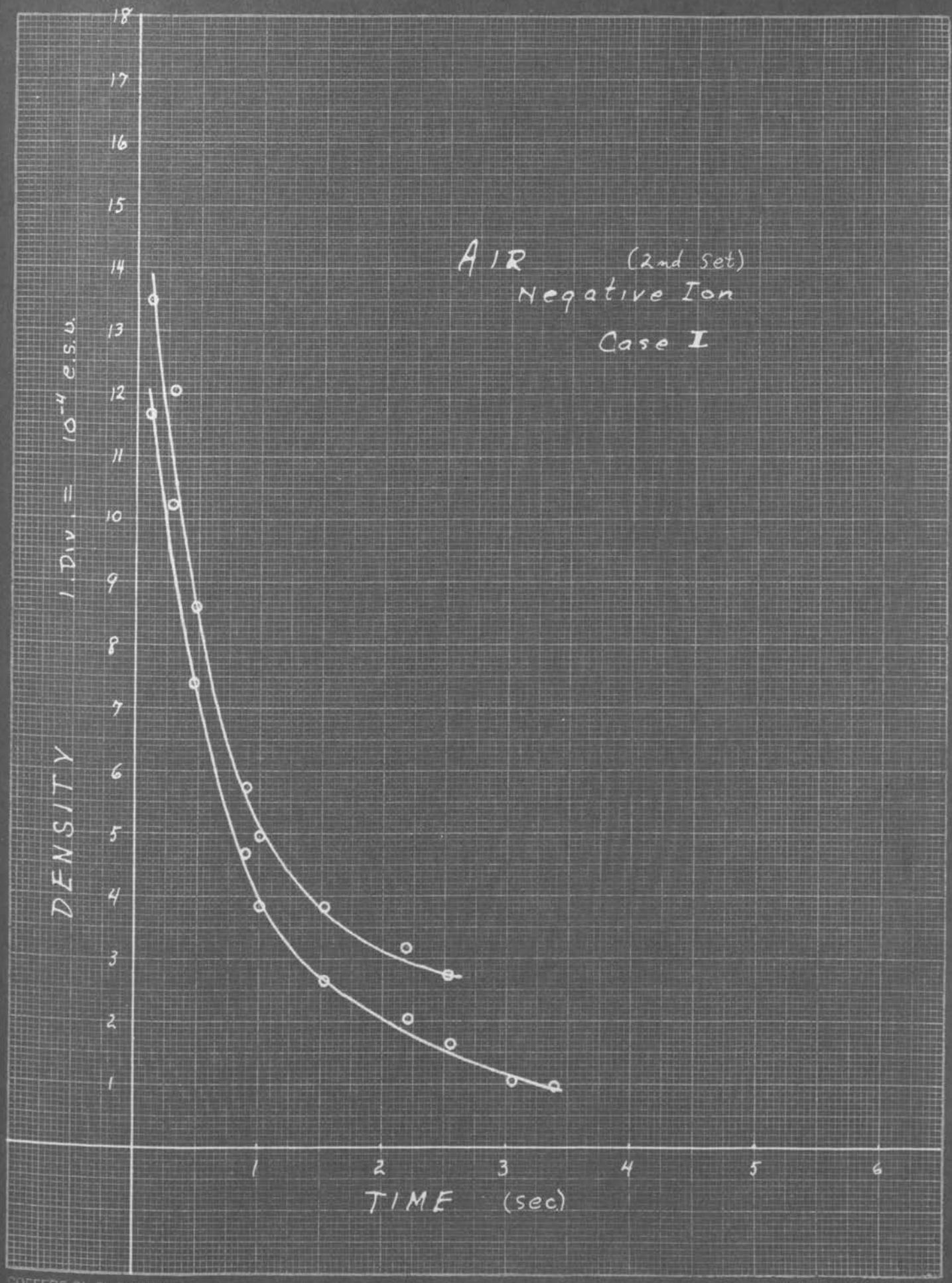
CURVES SHOWING VARIATION OF CHARGE DENSITY

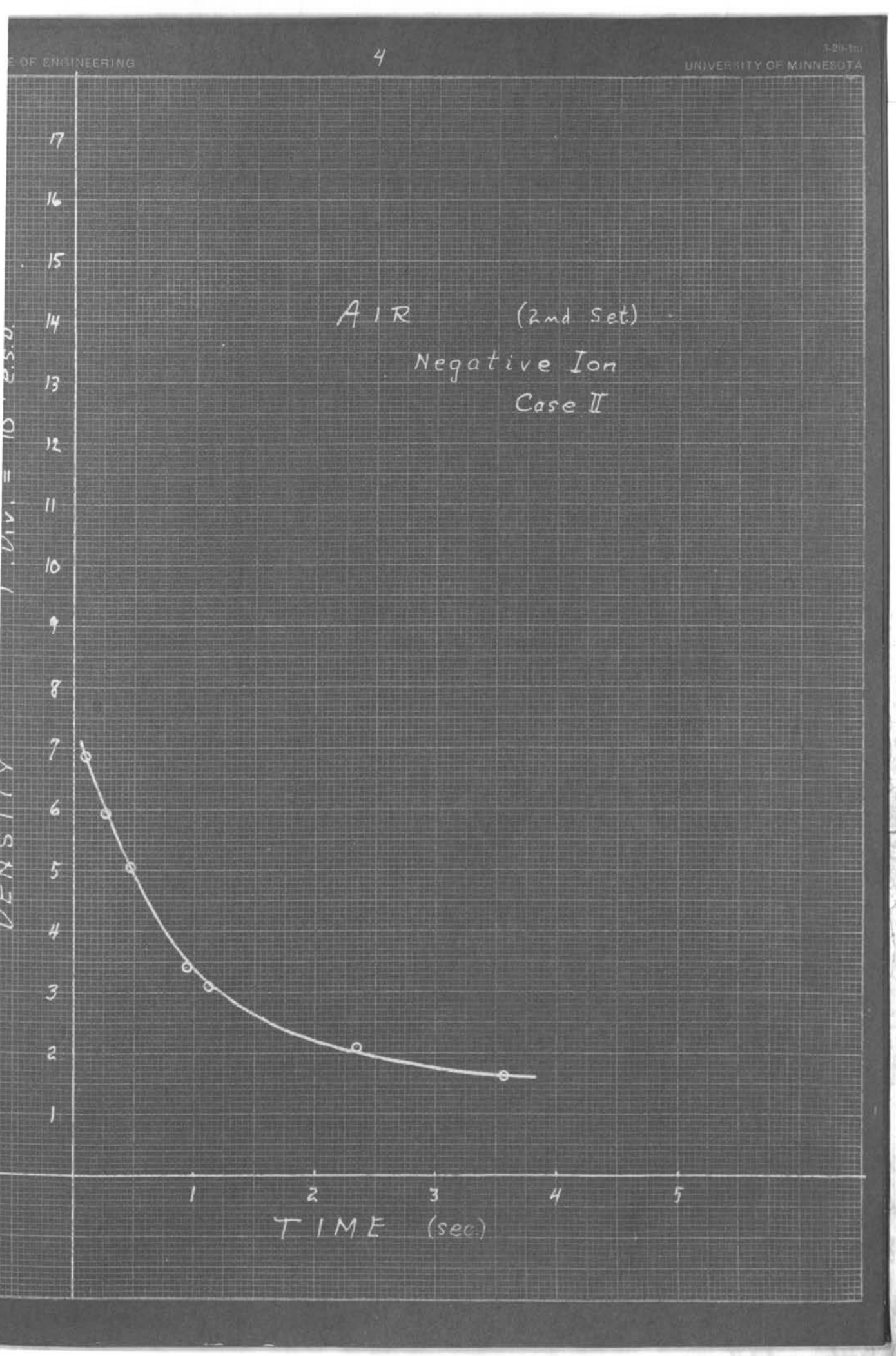
WITH TIME.

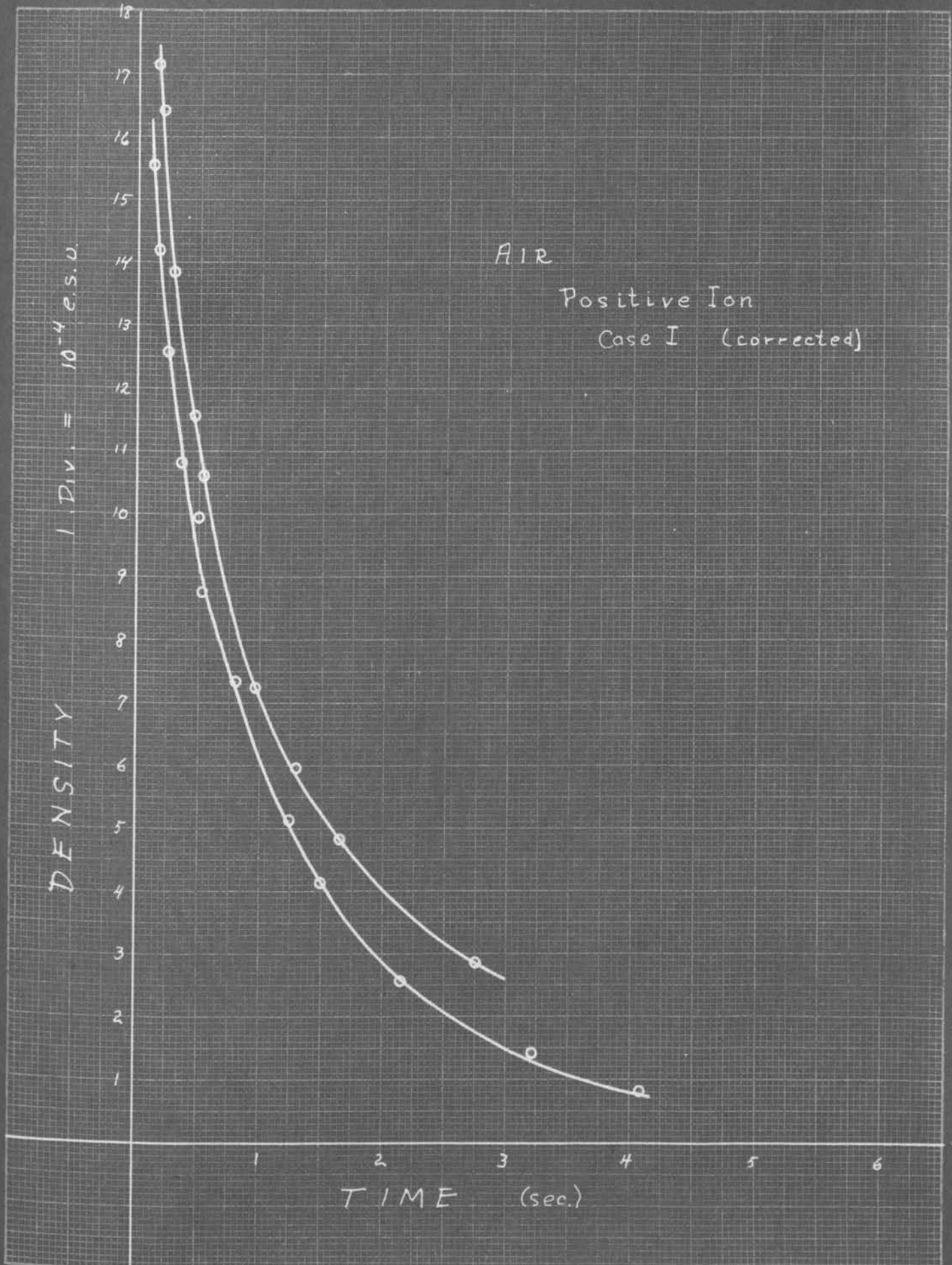
Upper Curves are corrected Curves for Case I.

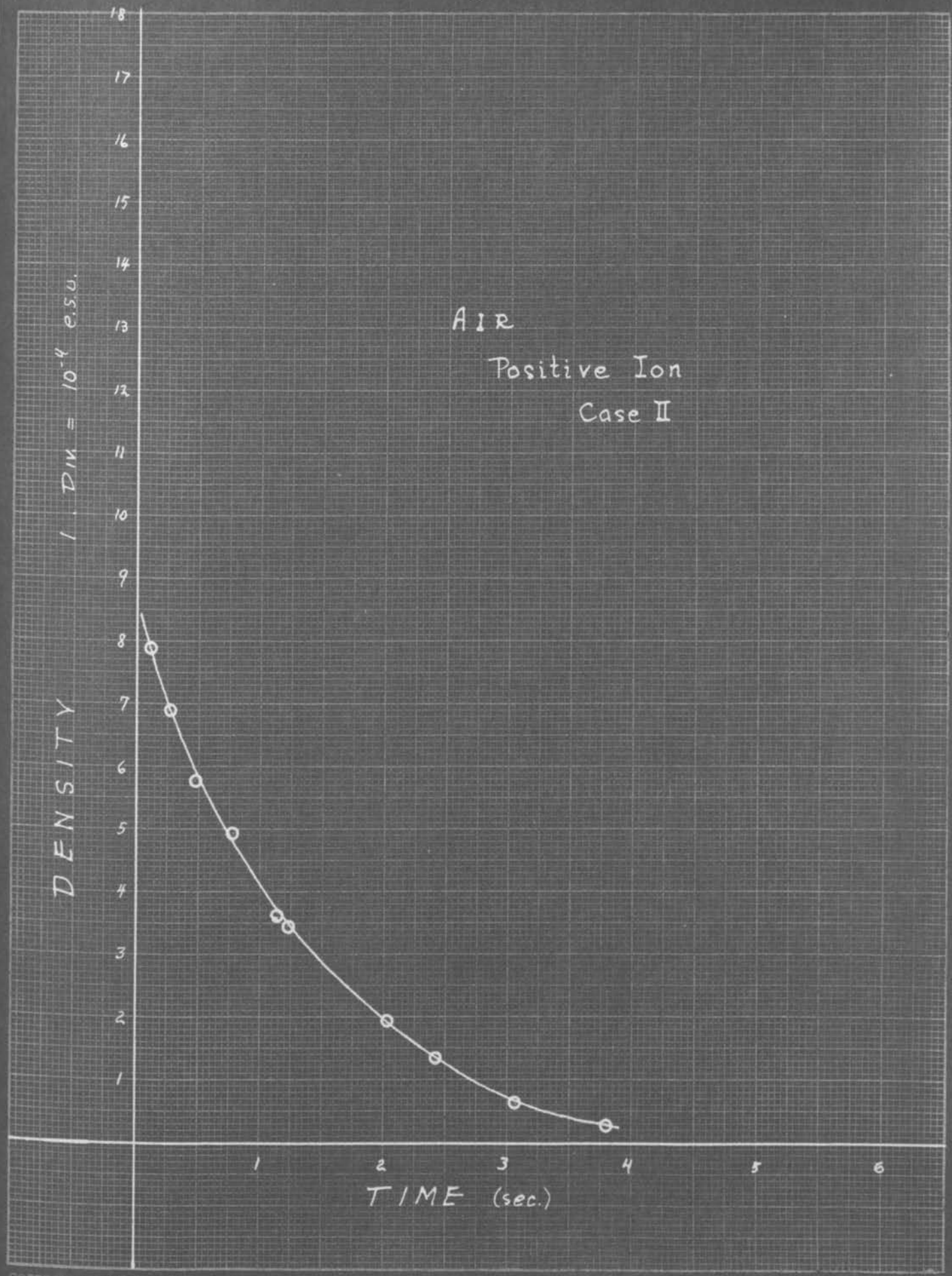

AIR (2nd Set)
Positive Ion
Case I
DENSITY 1 Div. = 10⁴ e.s.u.
TIME (sec.)
1
2
3
4
5

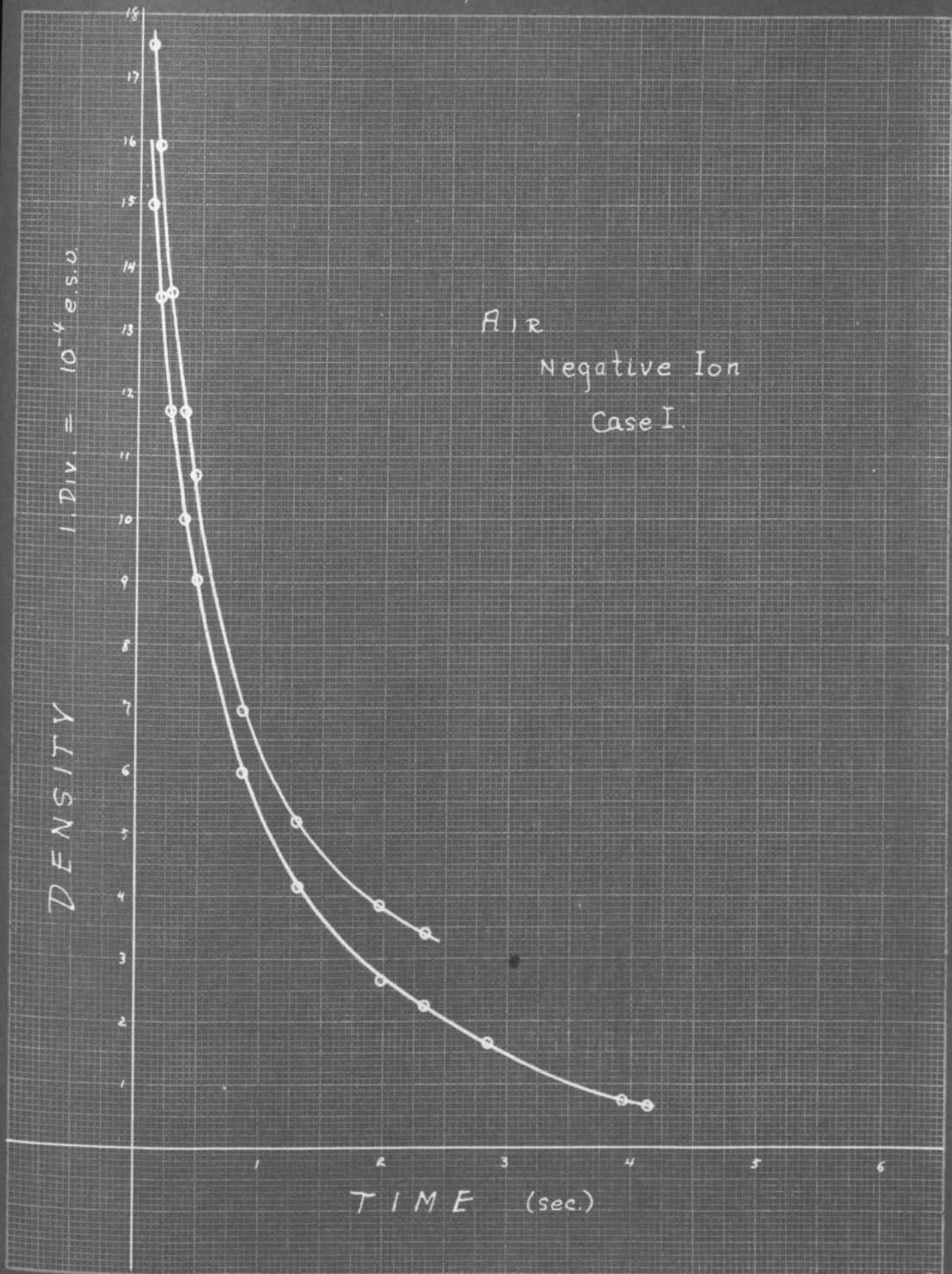


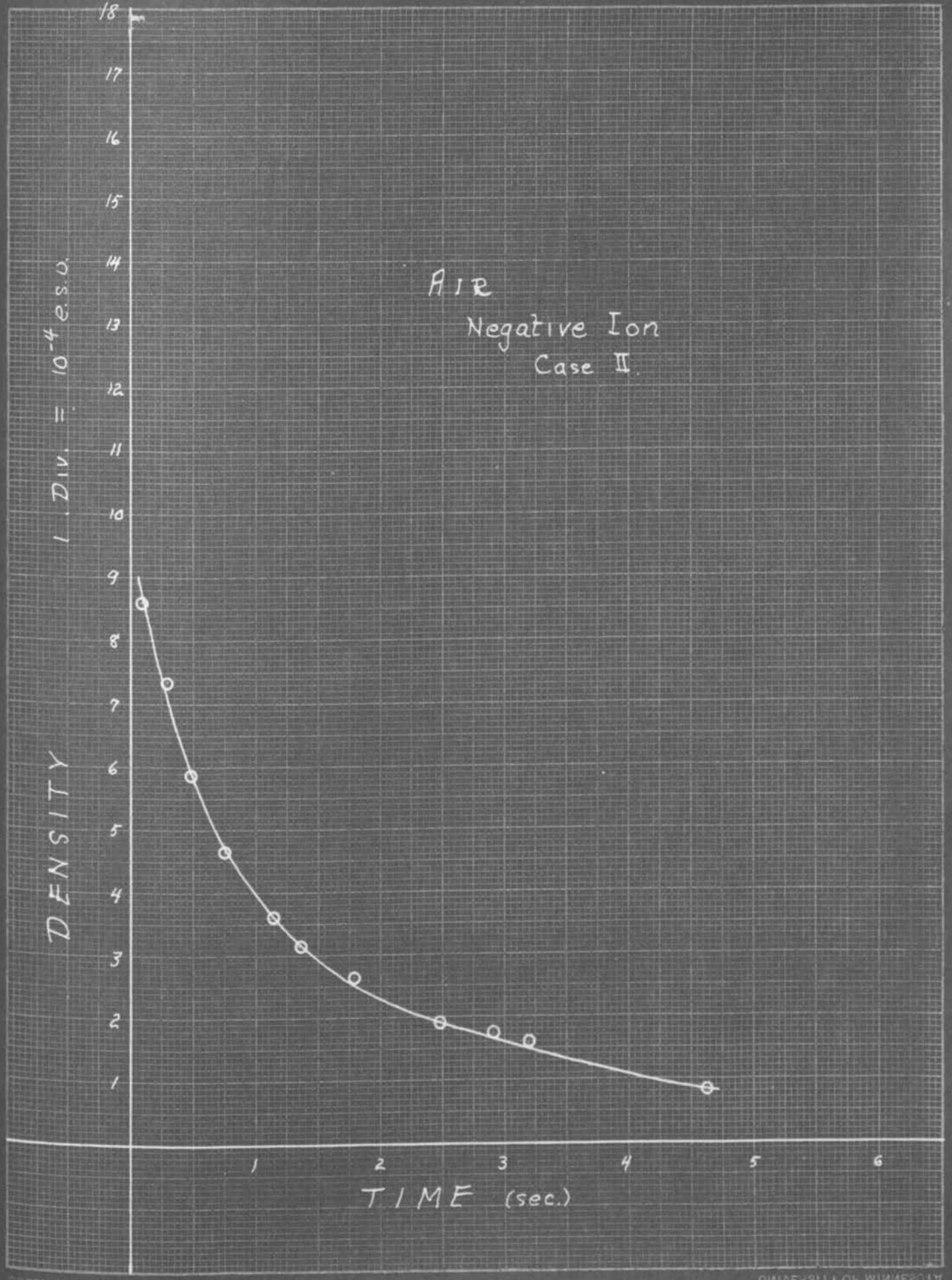


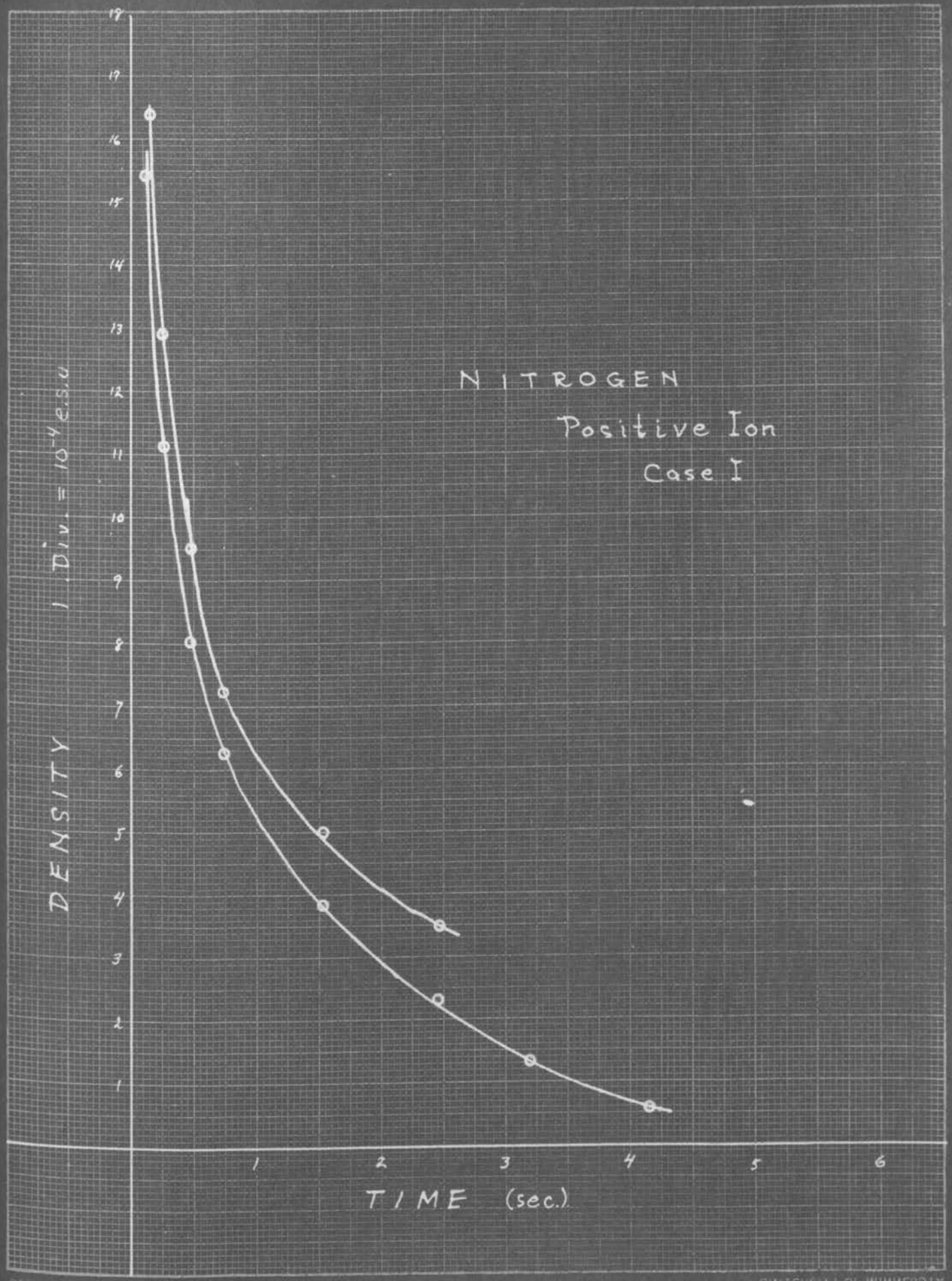

AIR (2nd Set)
Negative Ion
Case II
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
TIME (sec.)

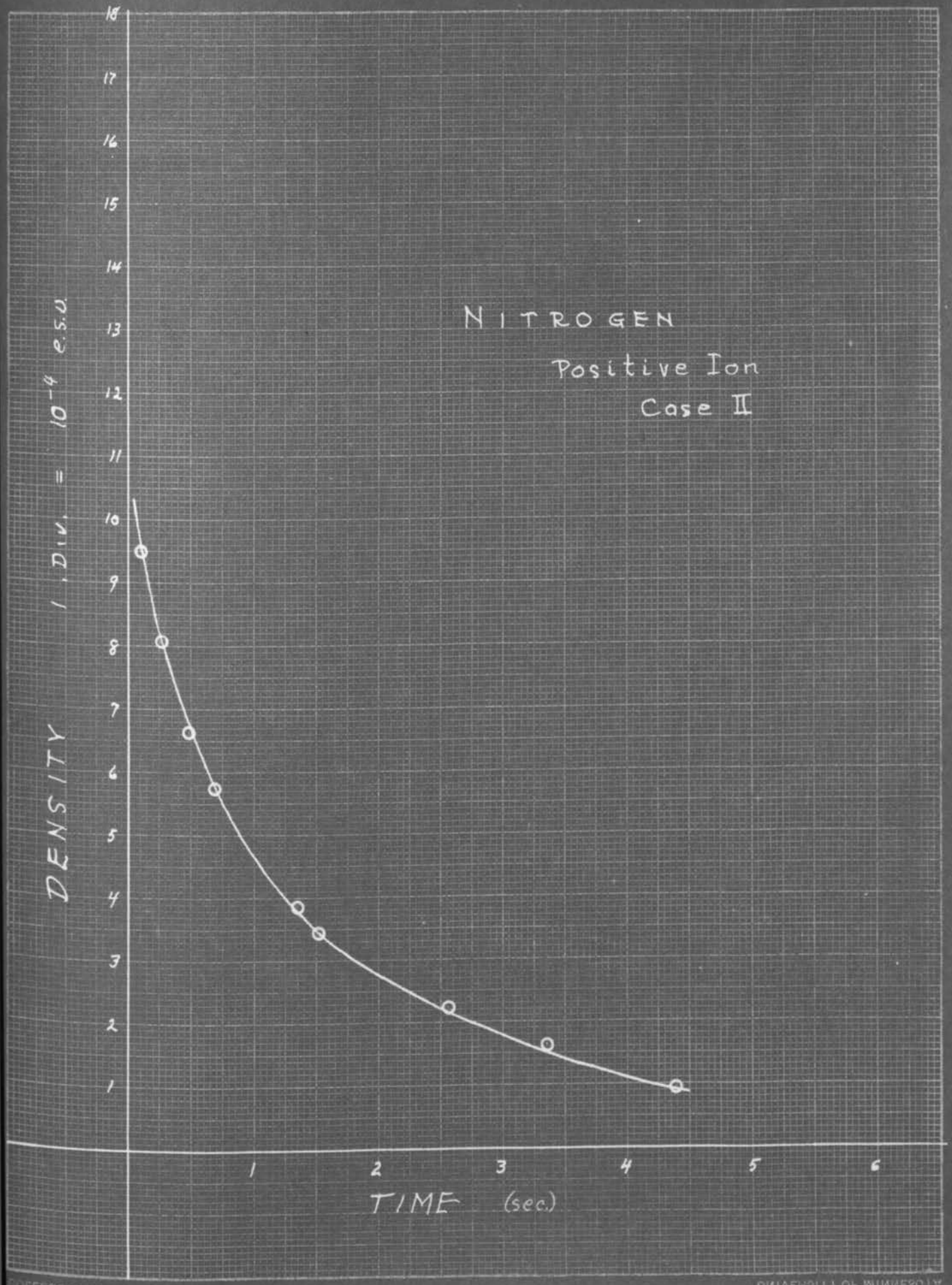

AIR
Positive Ion
Case I (corrected)
DENSITY 1 Div. = 10^{-4} e.s.u.
TIME (sec.)
1
2
3
4
5
6

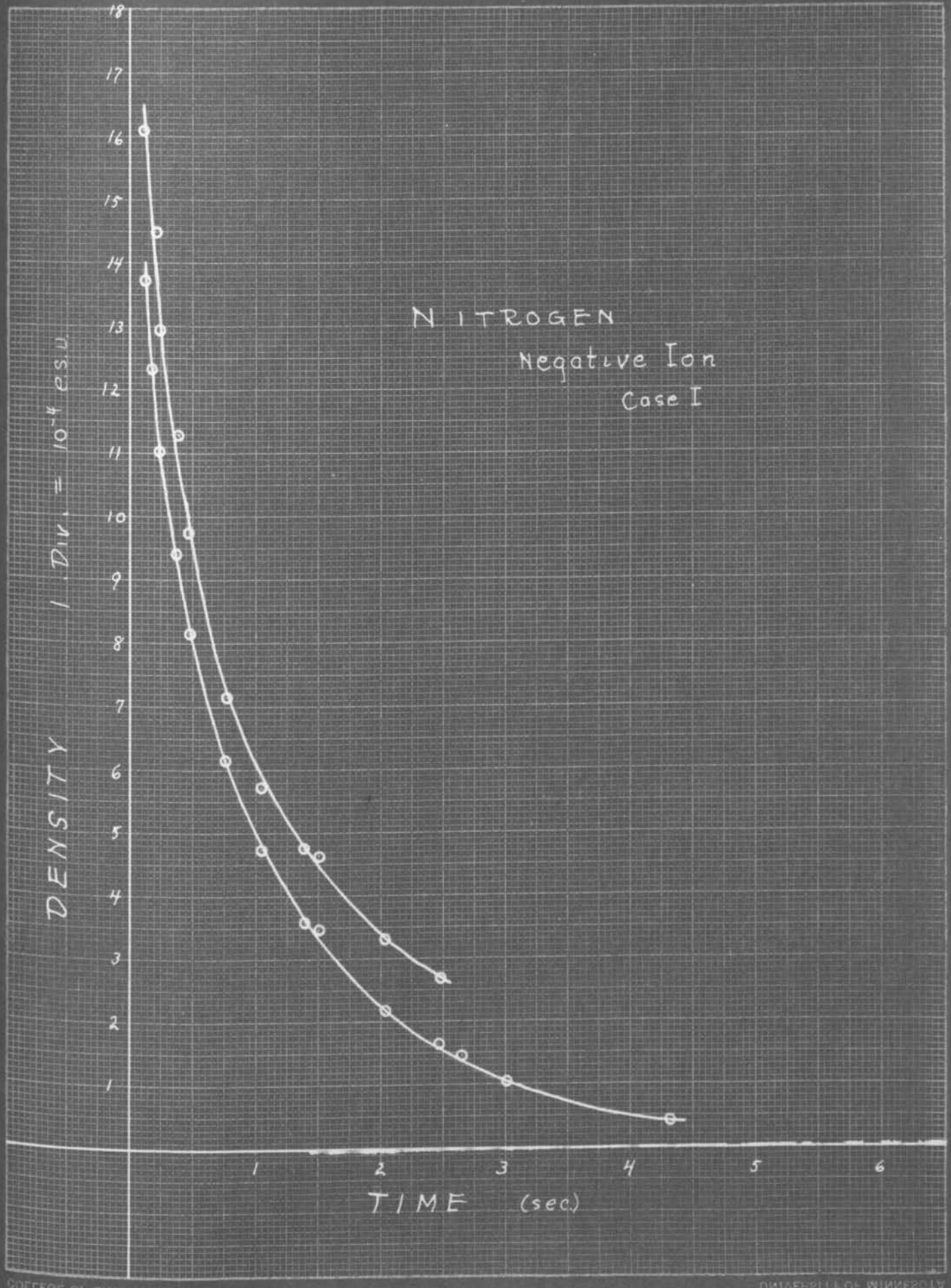


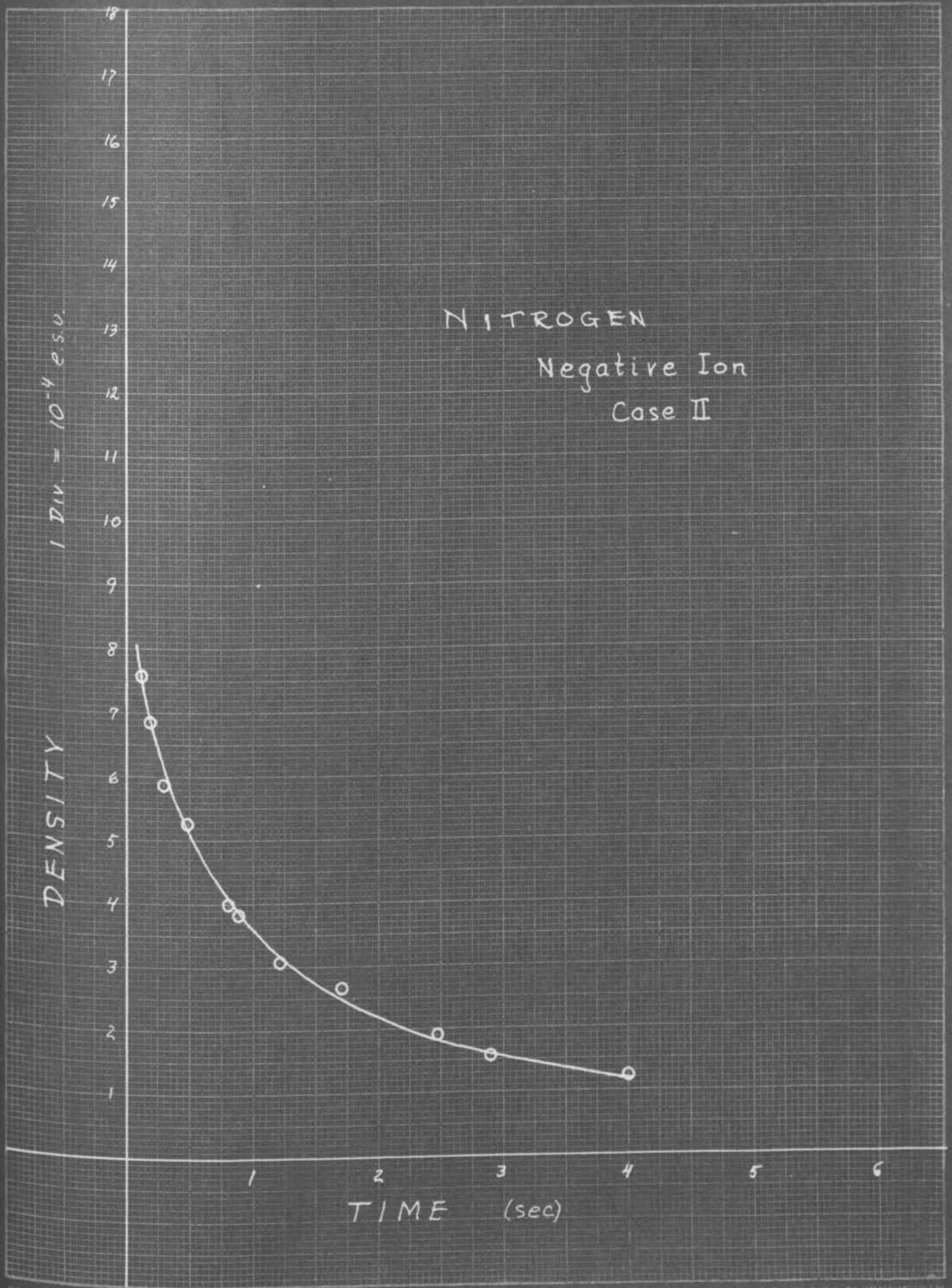


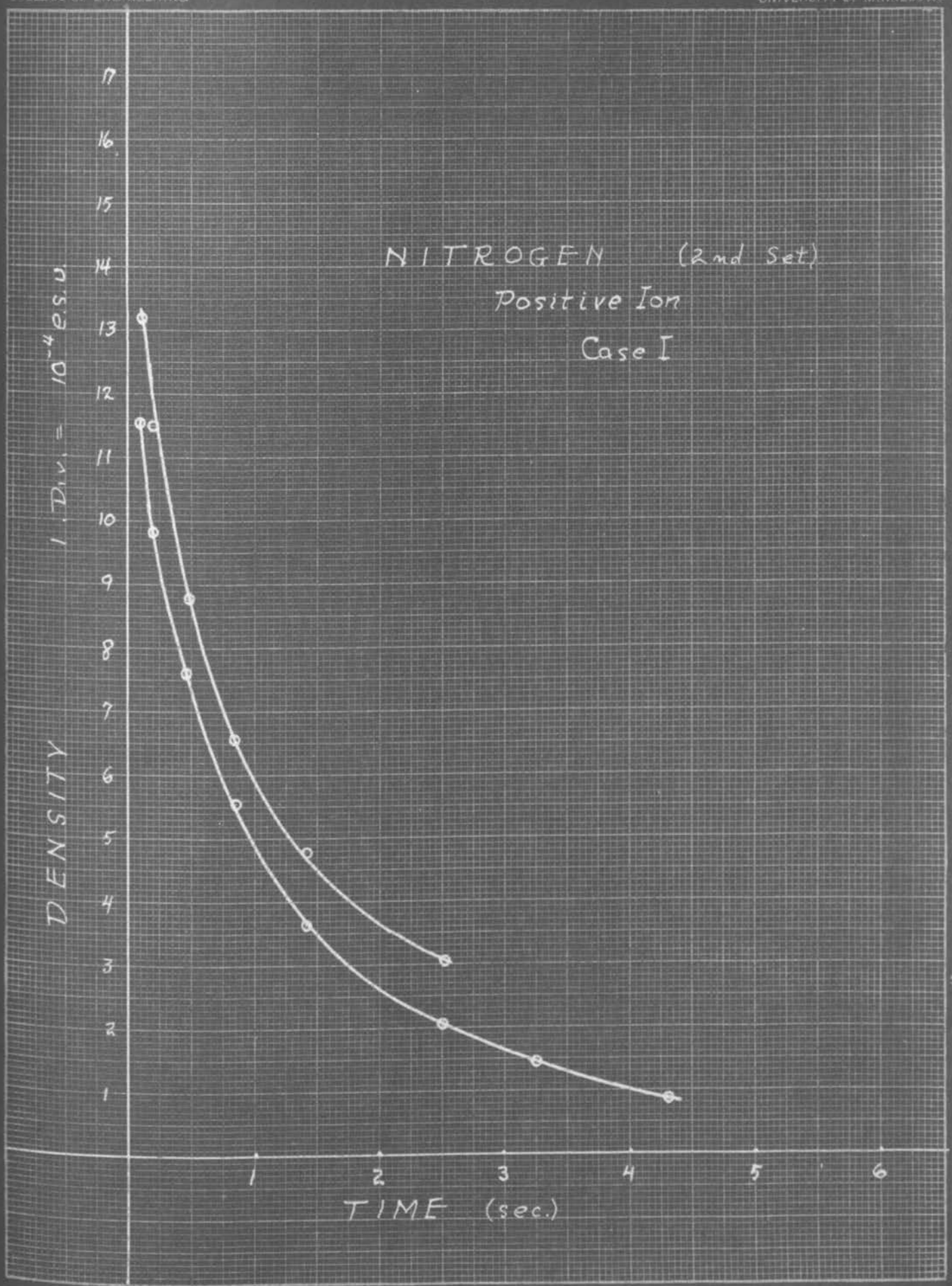


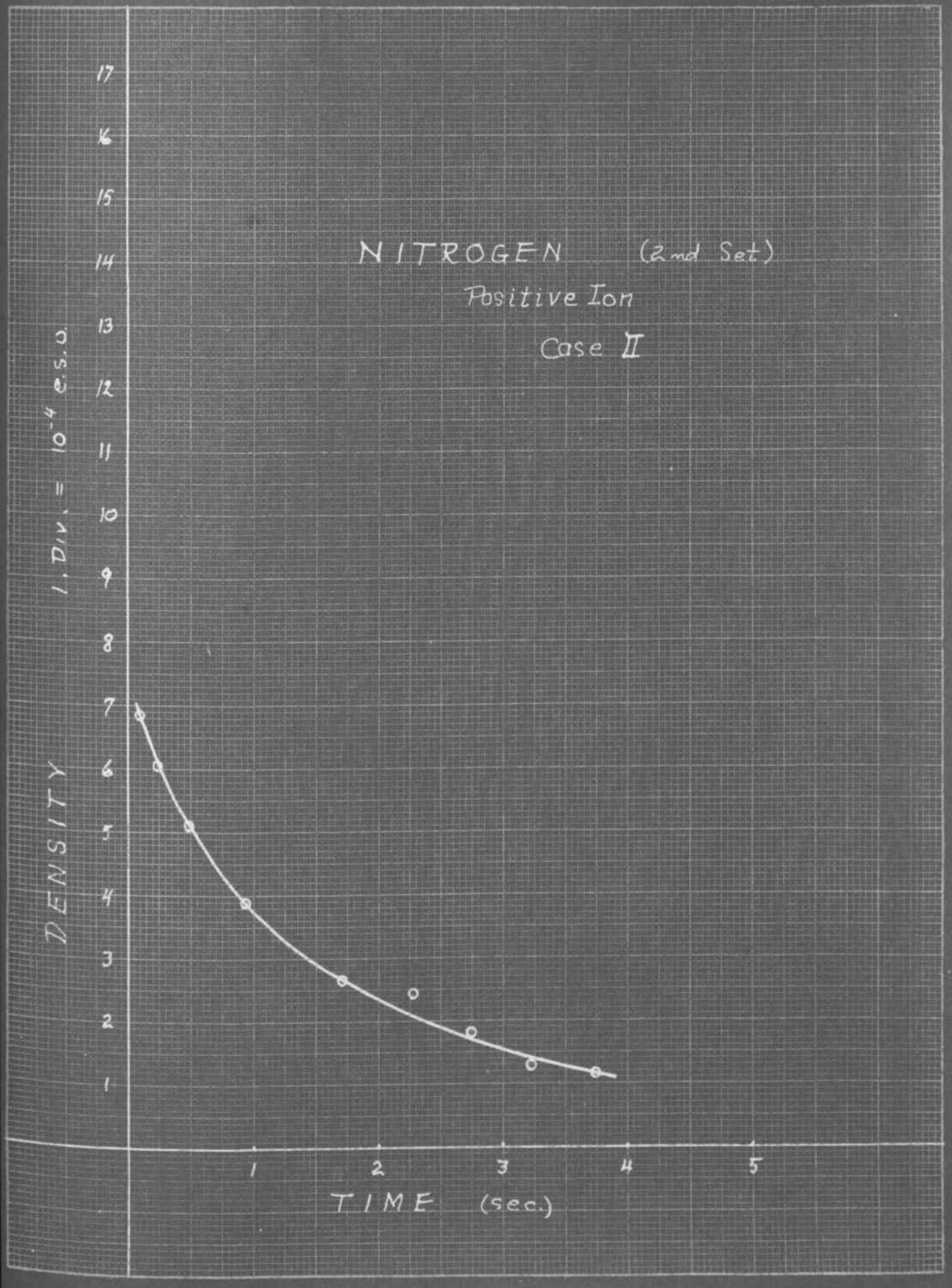

NITROGEN
Positive Ion
Case I
DENSITY 1 Div. = 10⁴ e.s.u.
TIME (sec.)
1
2
3
4
5
6

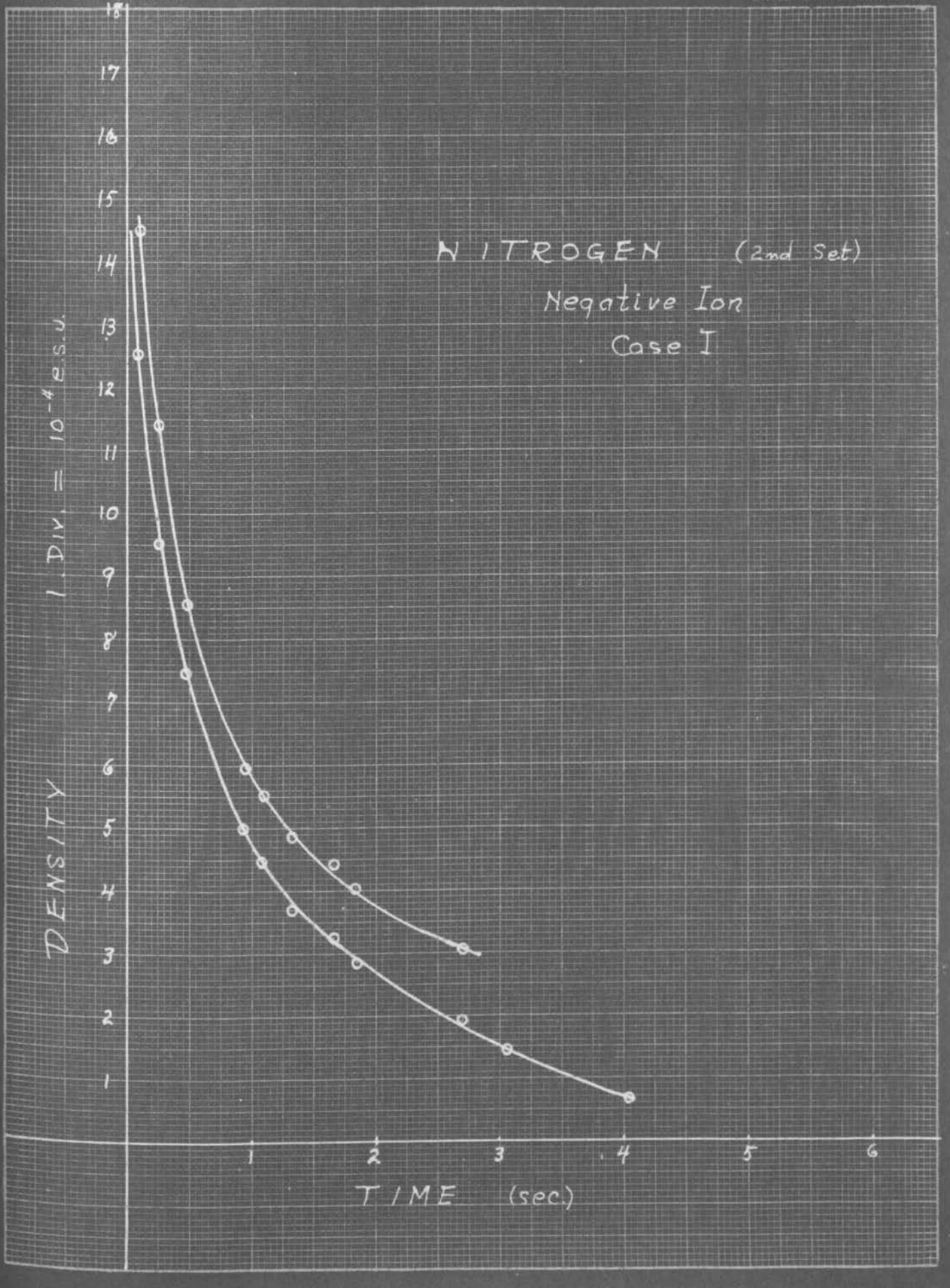


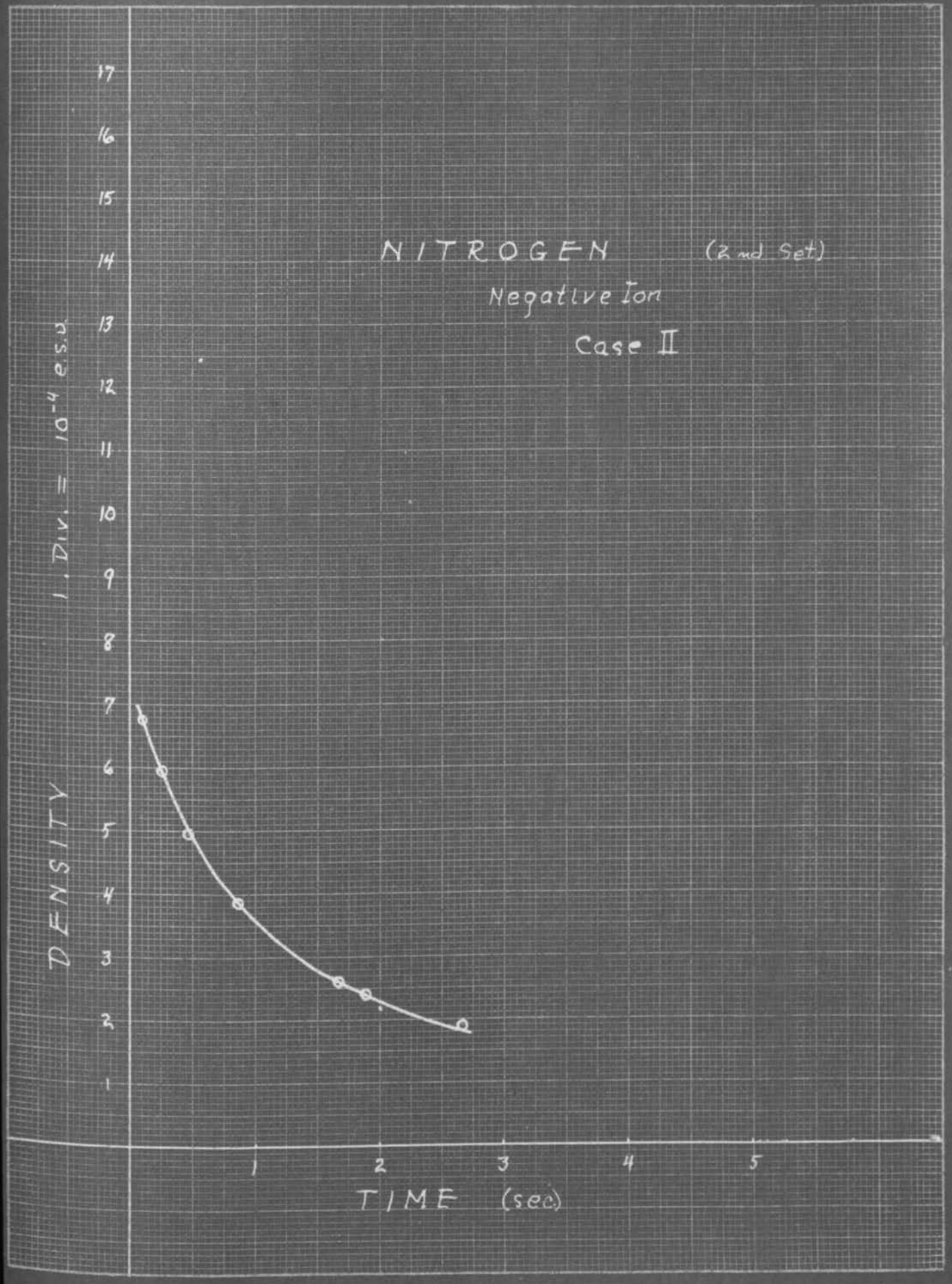


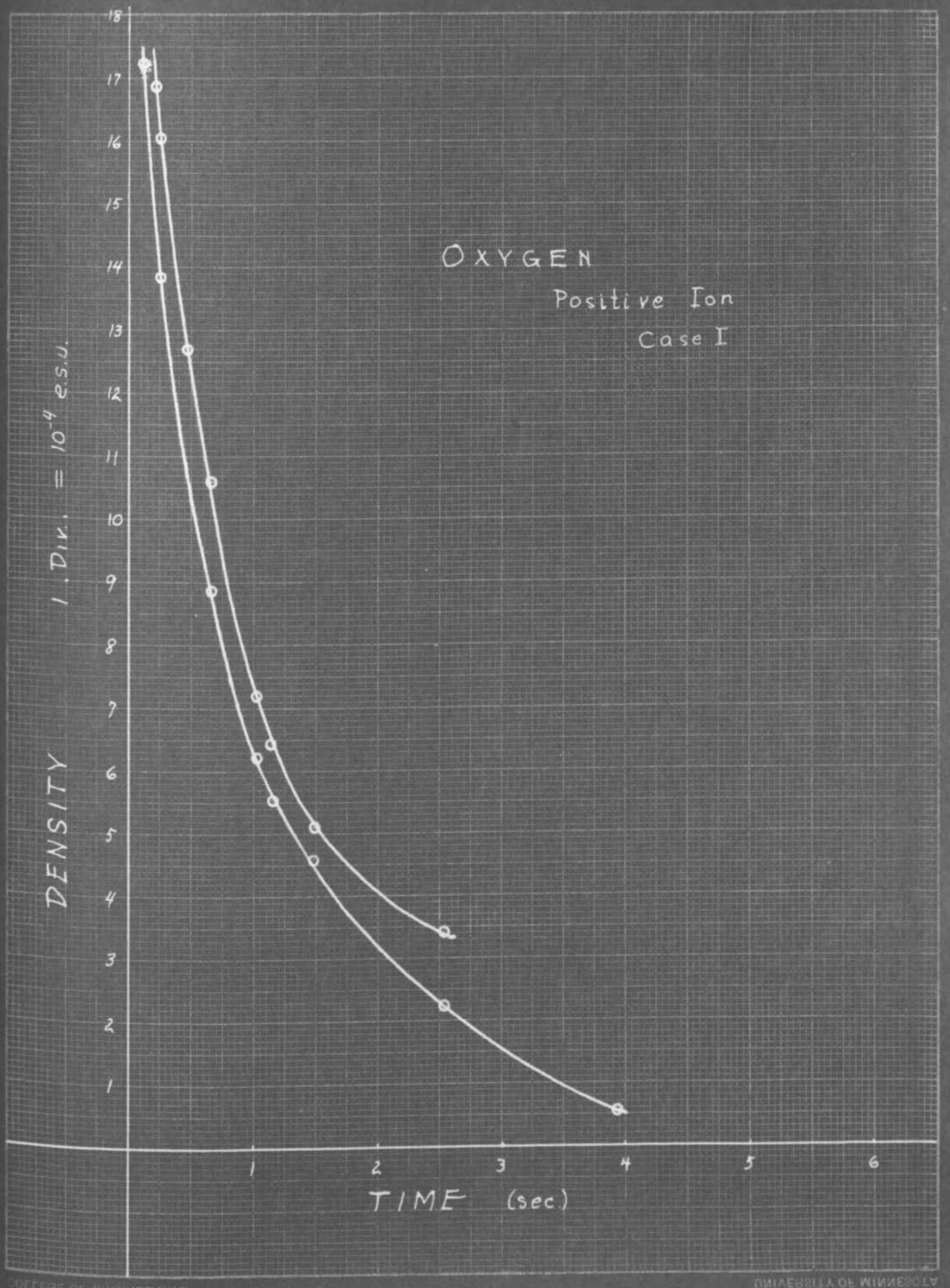


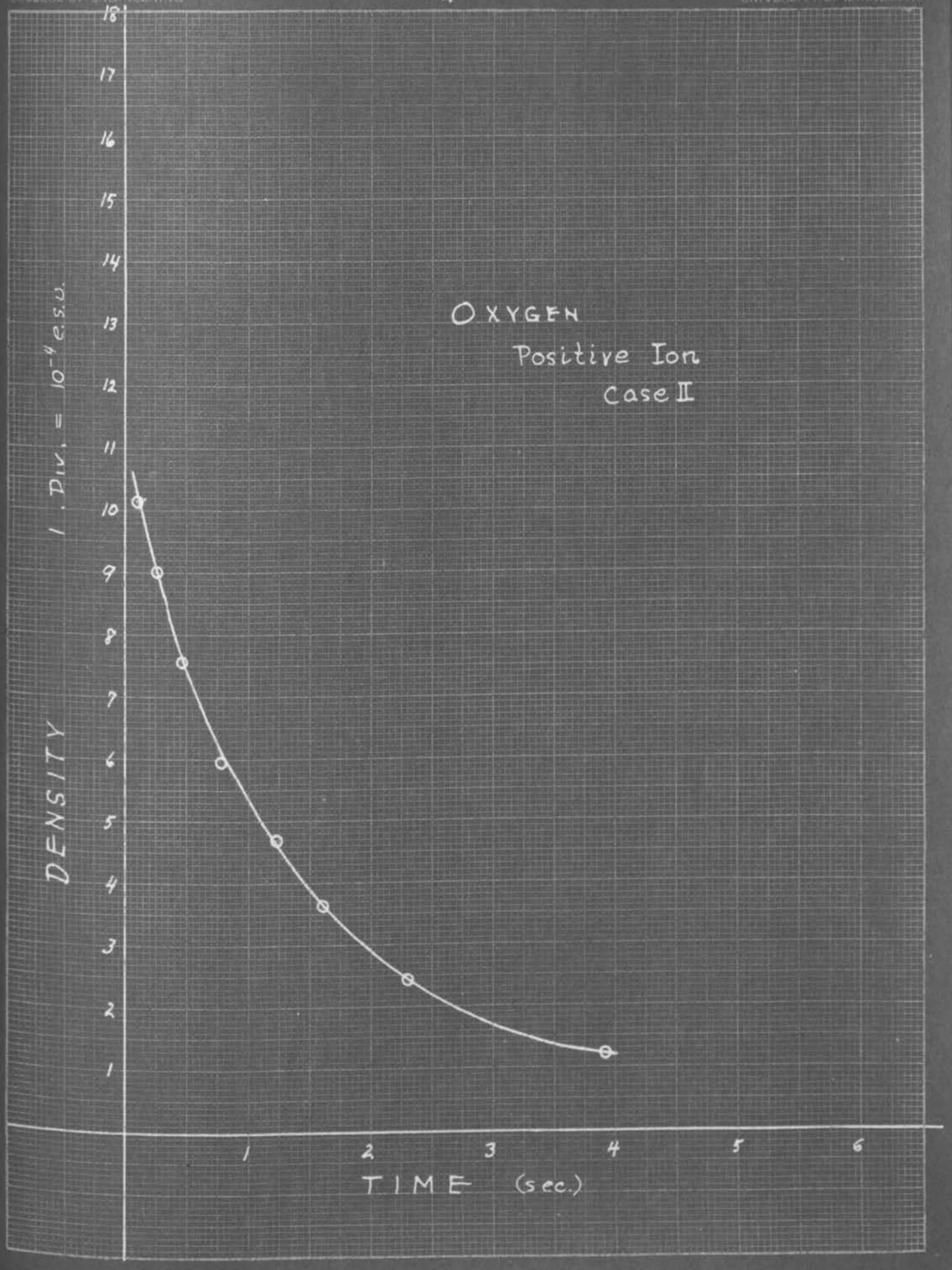

NITROGEN (2nd Set)
Positive Ion
Case I
DENSITY 1 Div. = 10^{-4} e.s.u.
TIME (sec.)
1
2
3
4
5
6
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

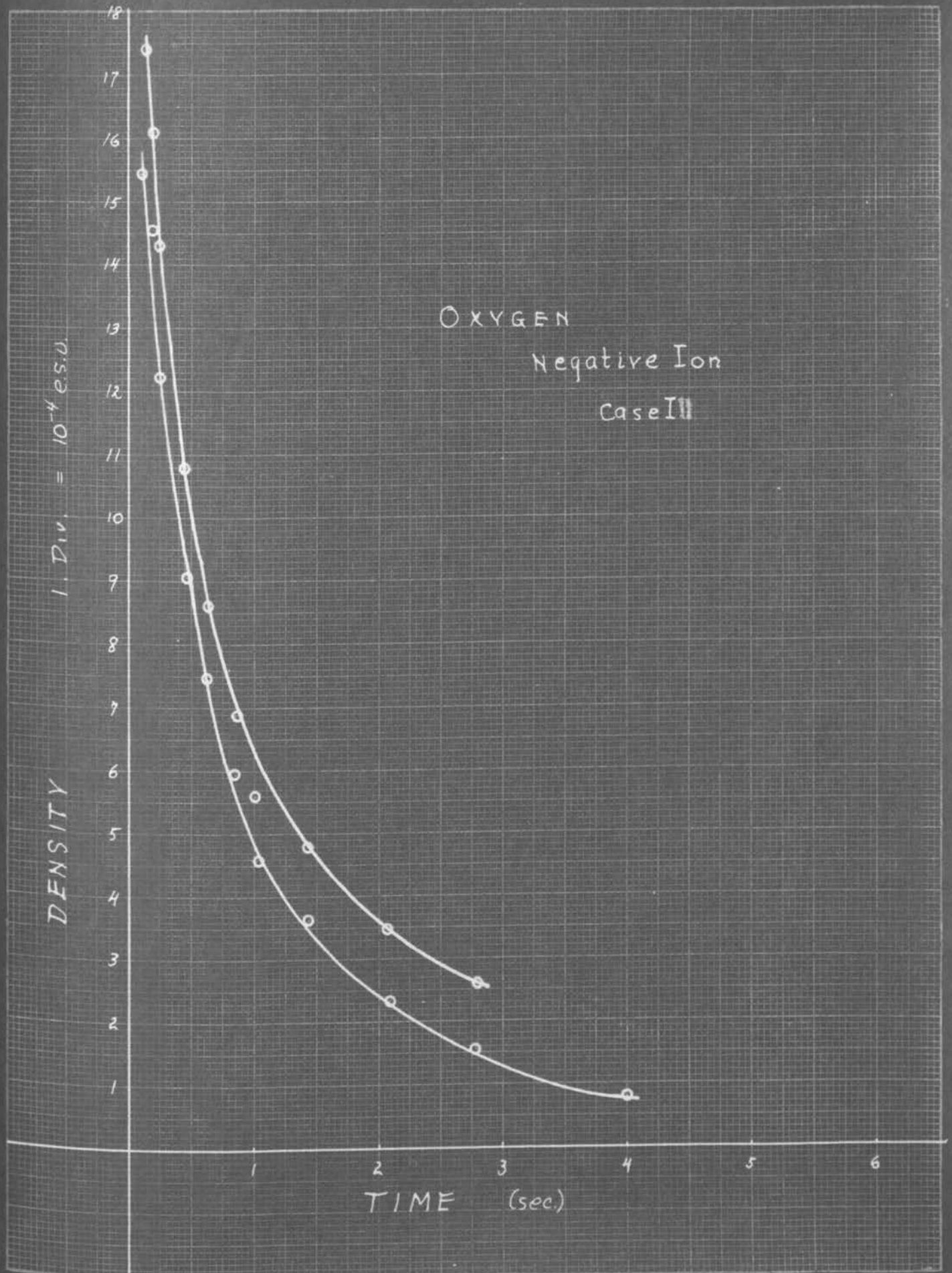

NITROGEN (2nd Set)
Positive Ion
Case II
DENSITY 1 Div. = 10⁻⁴ e.s.u.
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
TIME (sec.)

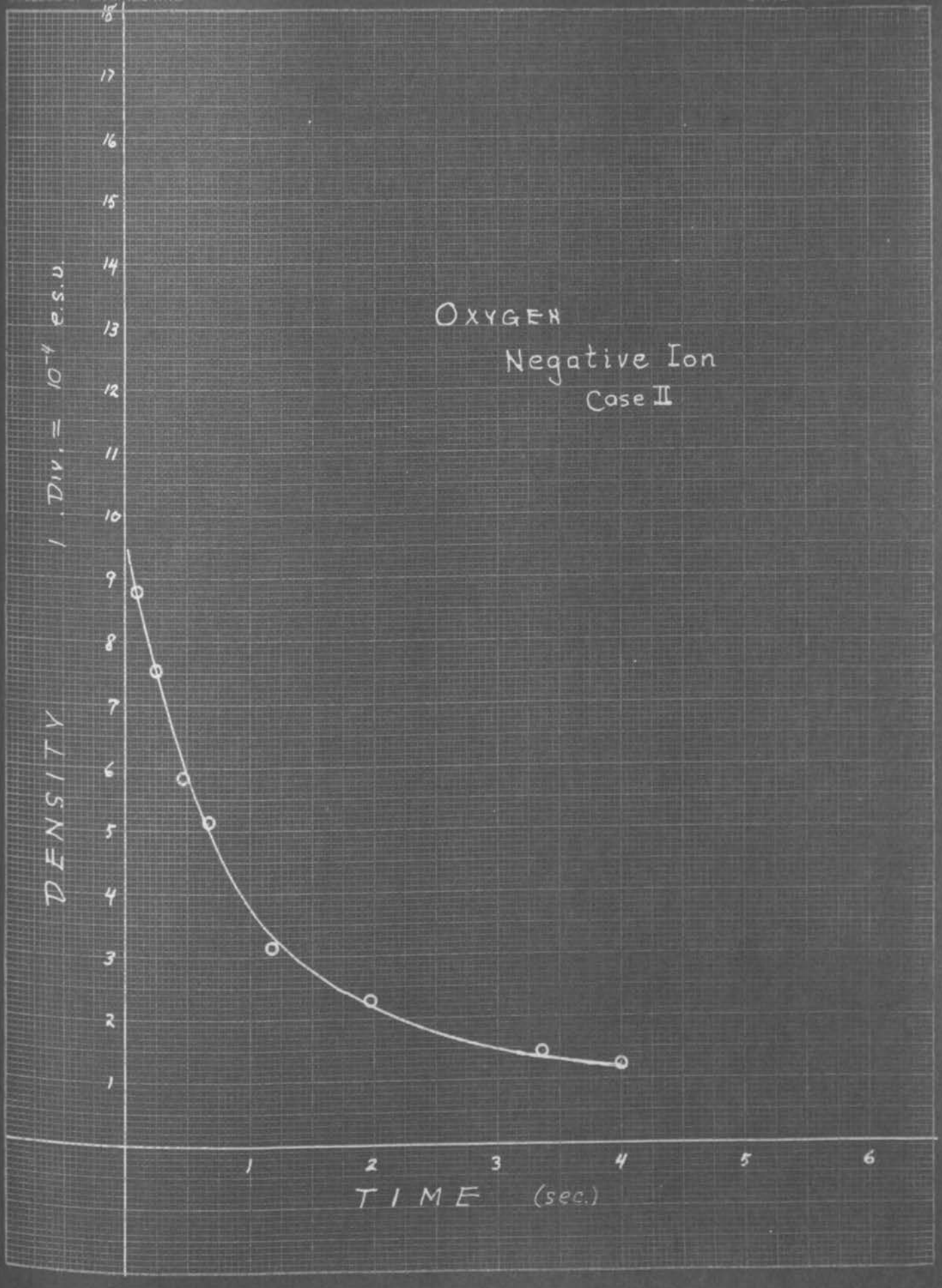

NITROGEN (2nd Set)
Negative Ion
Case I
DENSITY
1 DIV. = 10⁻⁴ e.s.u.
TIME (sec.)
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6

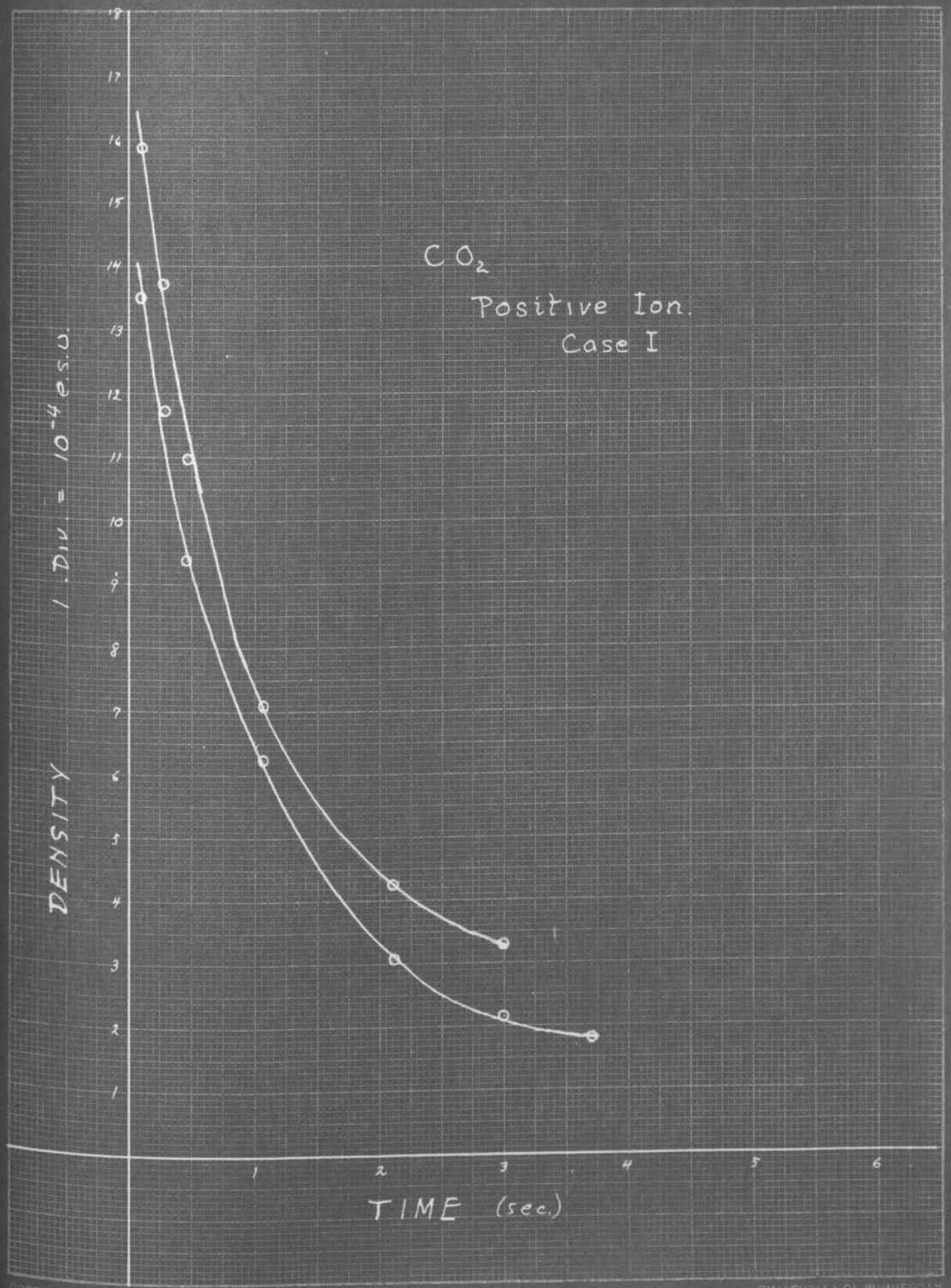

NITROGEN (2nd Set)
Negative Ion
Case II
DENSITY 1 Div. = 10-4 e.s.u.
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
TIME (sec.)

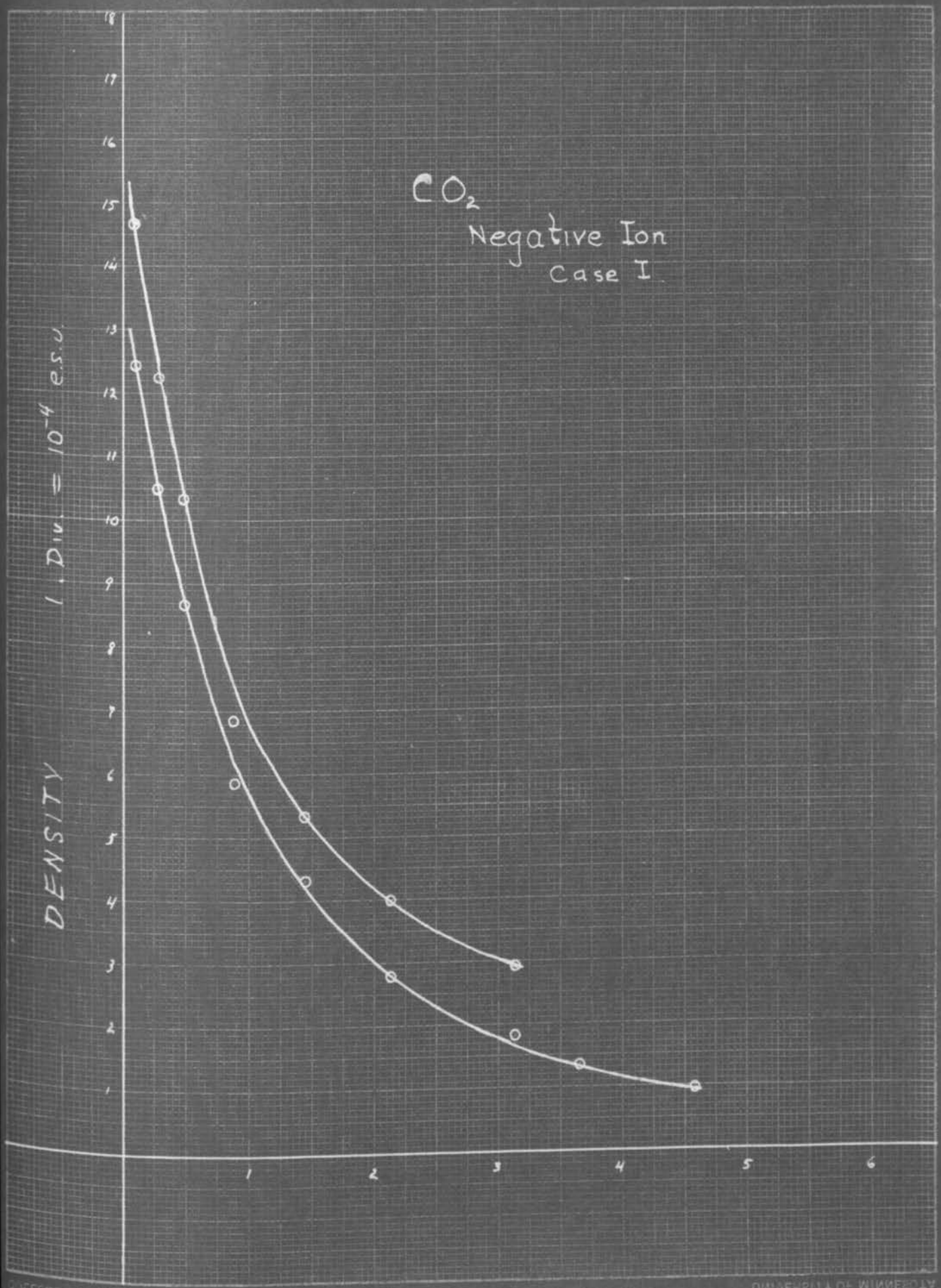


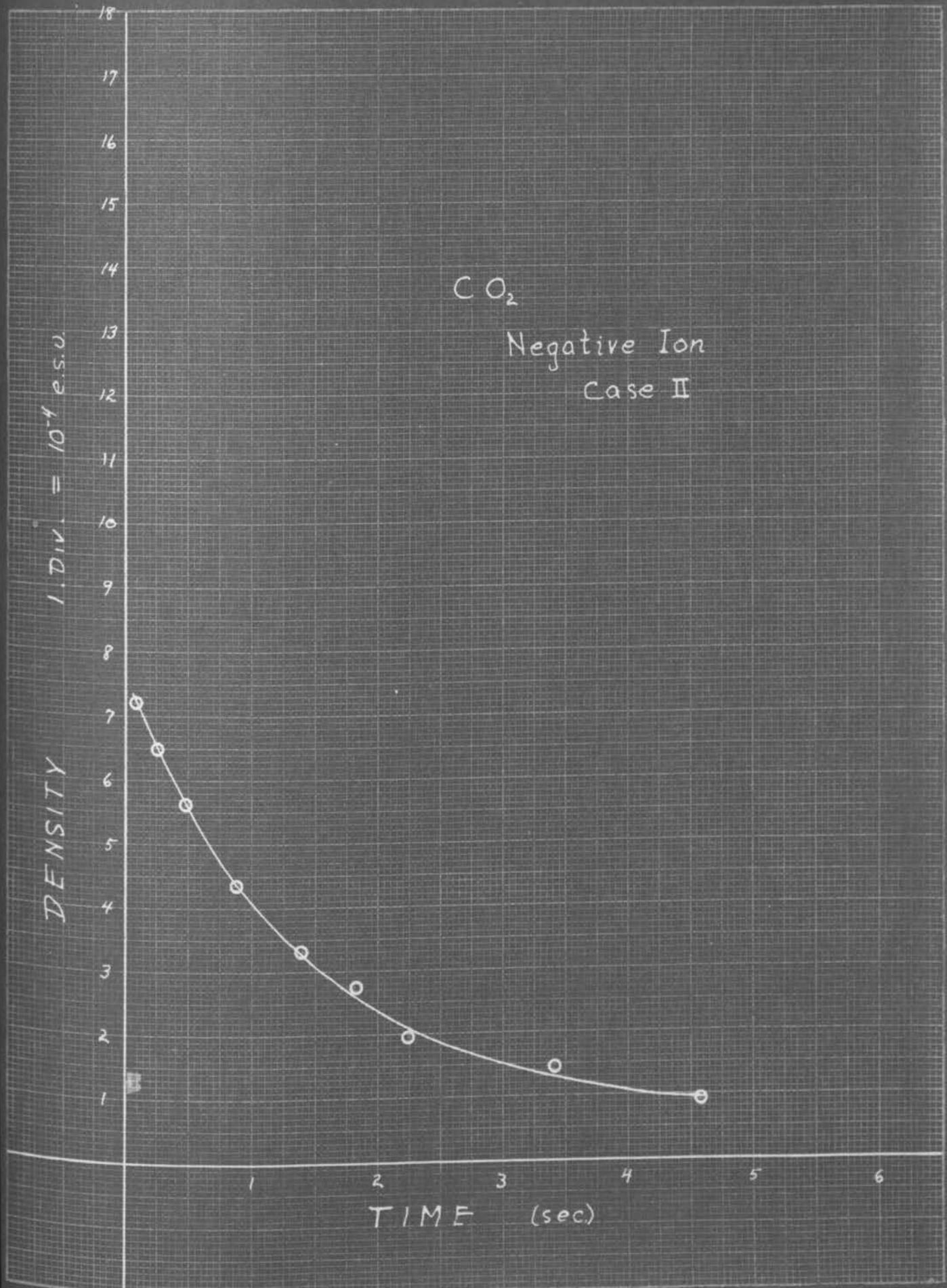

OXYGEN
Positive Ion
Case II
DENSITY
1 Div. = 10^{-4} e.s.u.
TIME (sec.)
1
2
3
4
5
6
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

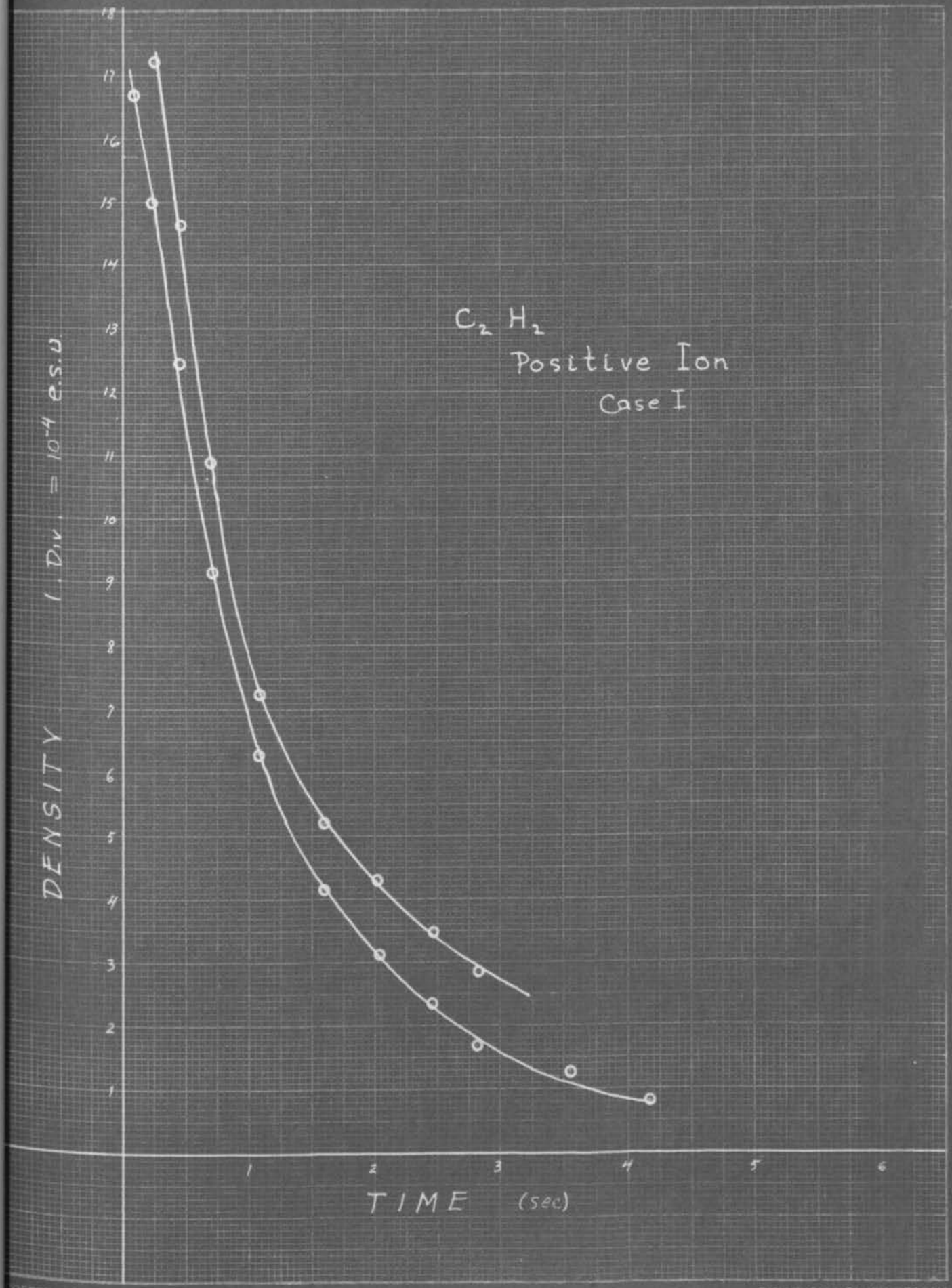


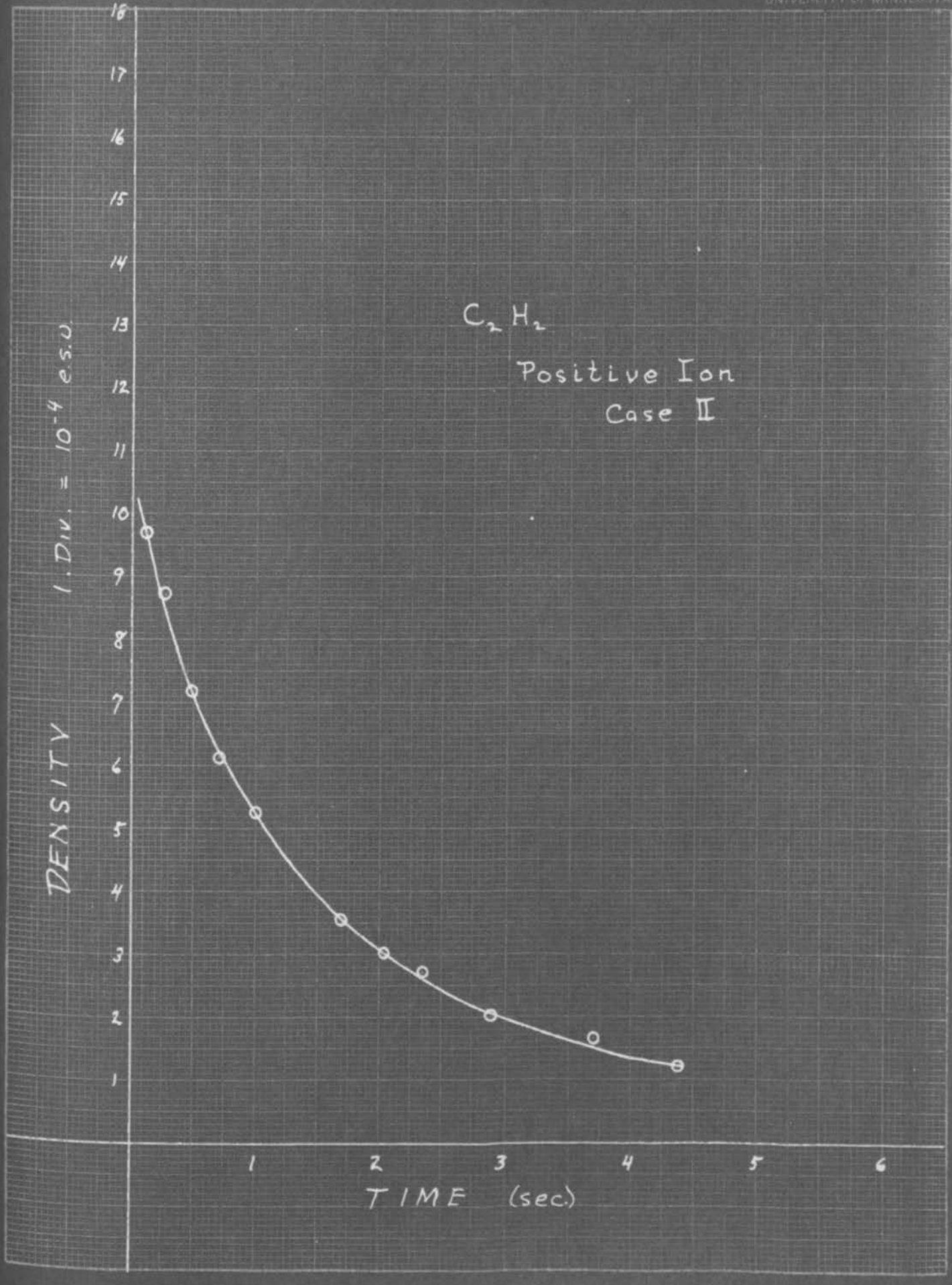

OXYGEN
Negative Ion
Case II
DENSITY 1 Div. = 10⁻⁴ e.s.u.
TIME (sec.)
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6

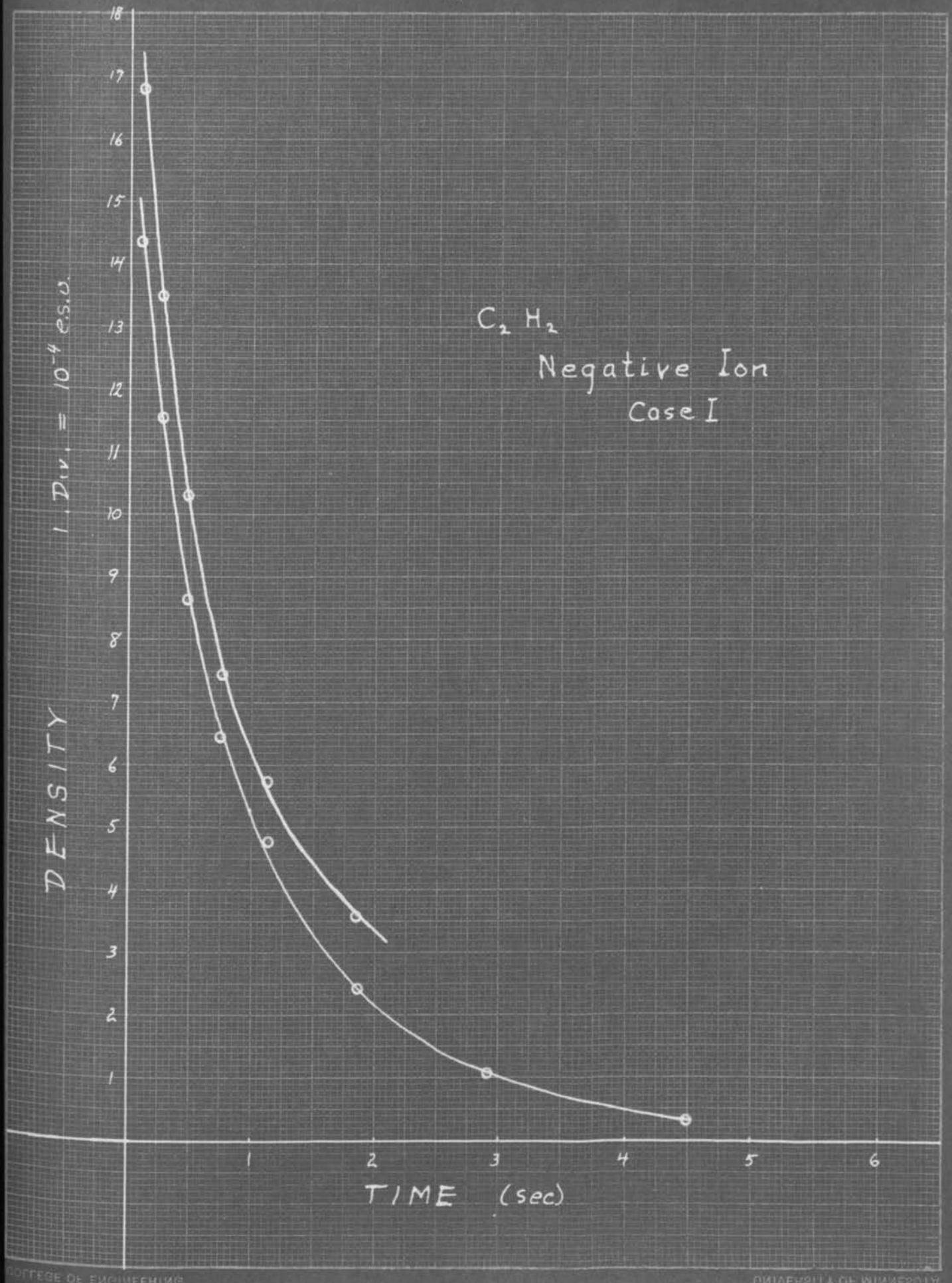


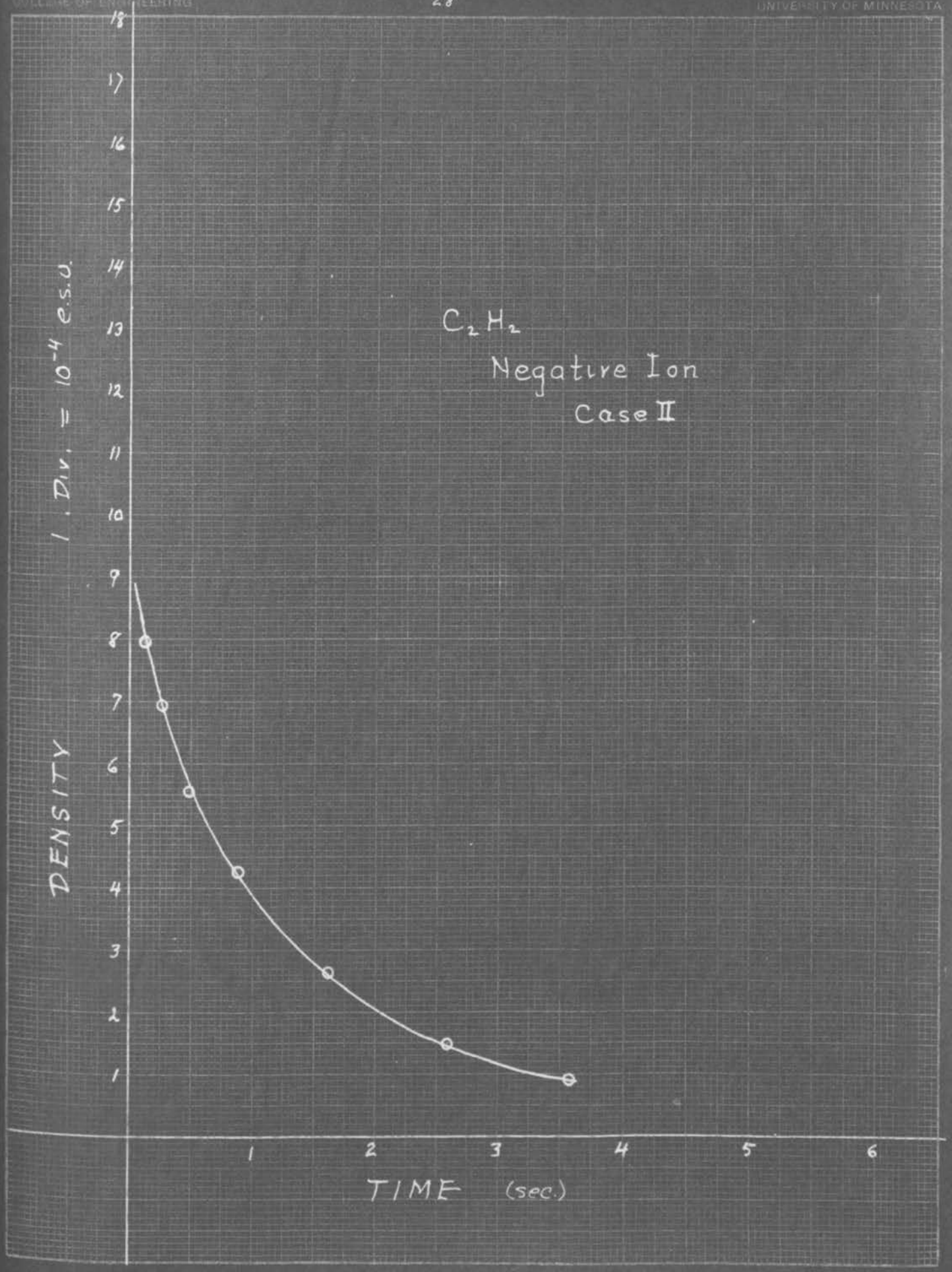


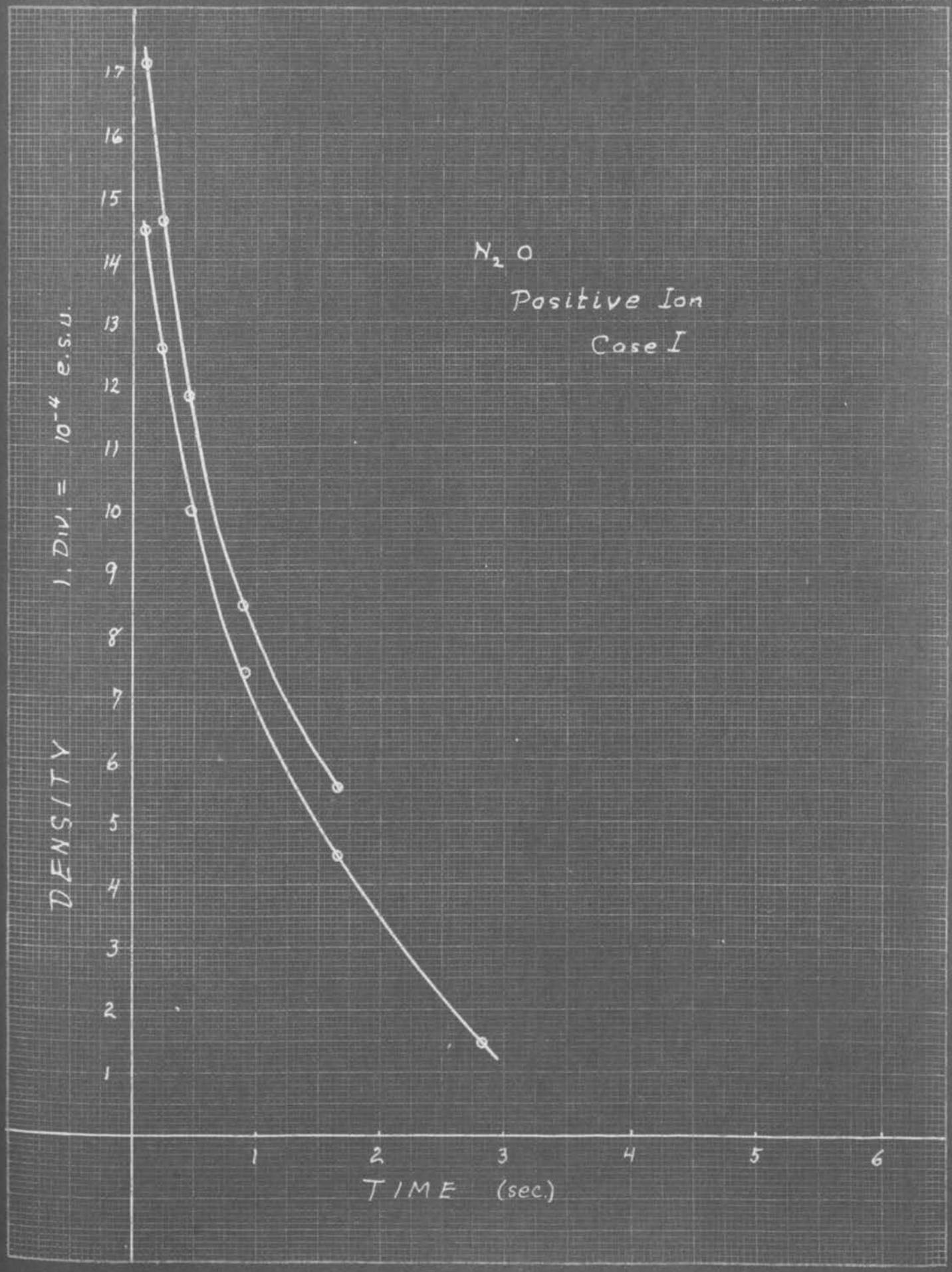


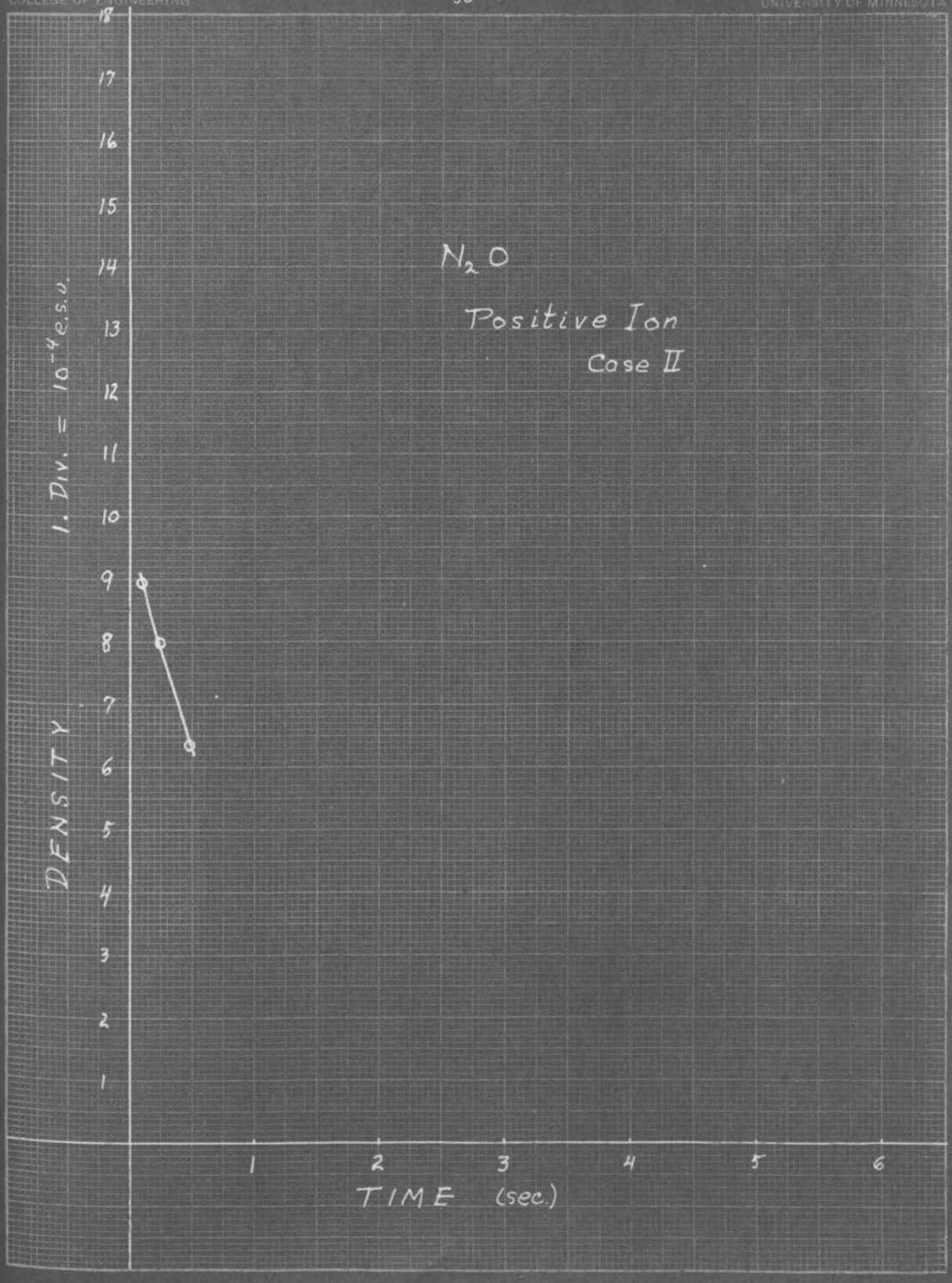


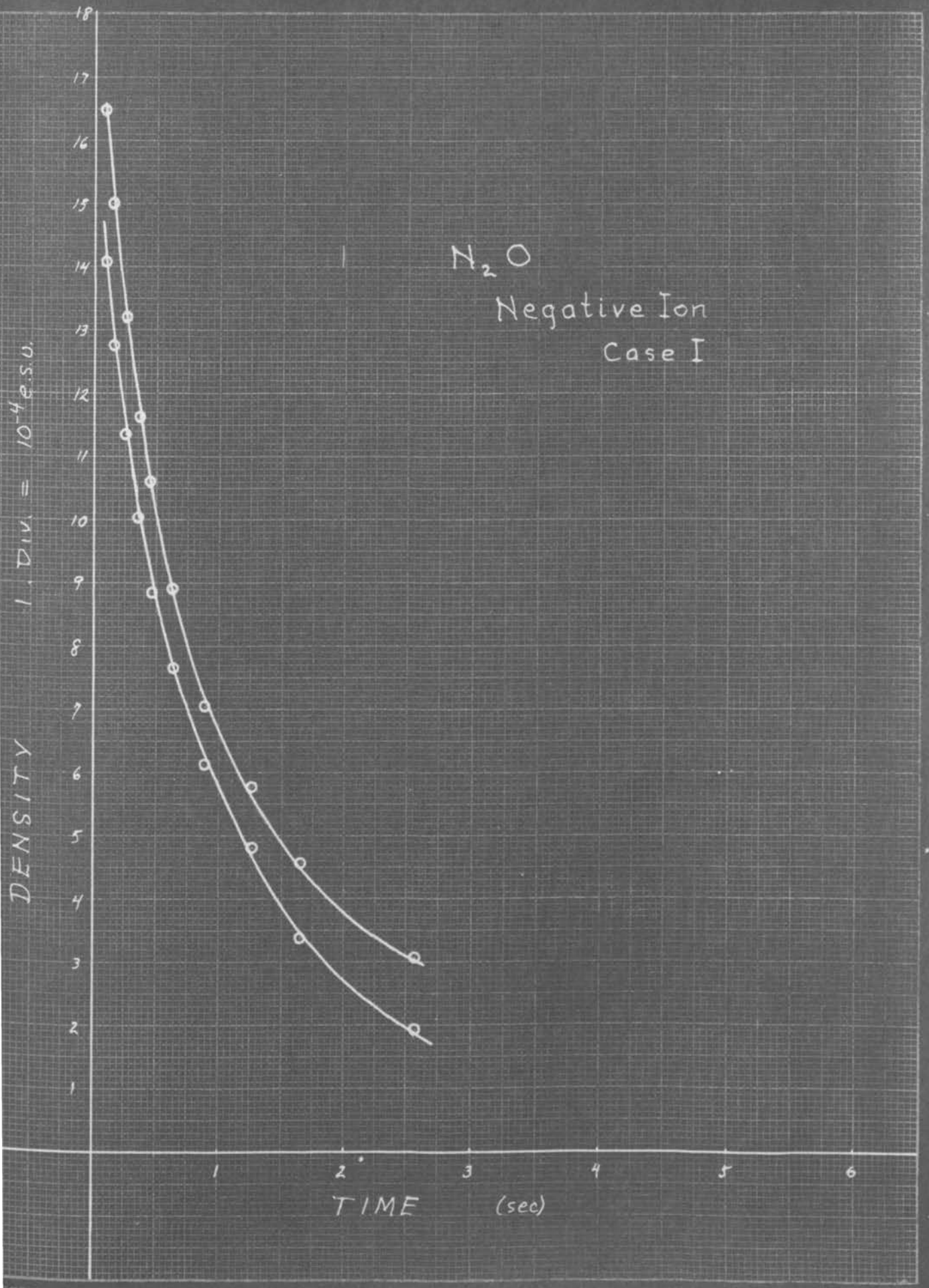

$C_2 H_2$
Positive Ion
Case II
DENSITY 1 Div. = 10^{-4} e.s.u.
TIME (sec.)
1
2
3
4
5
6
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

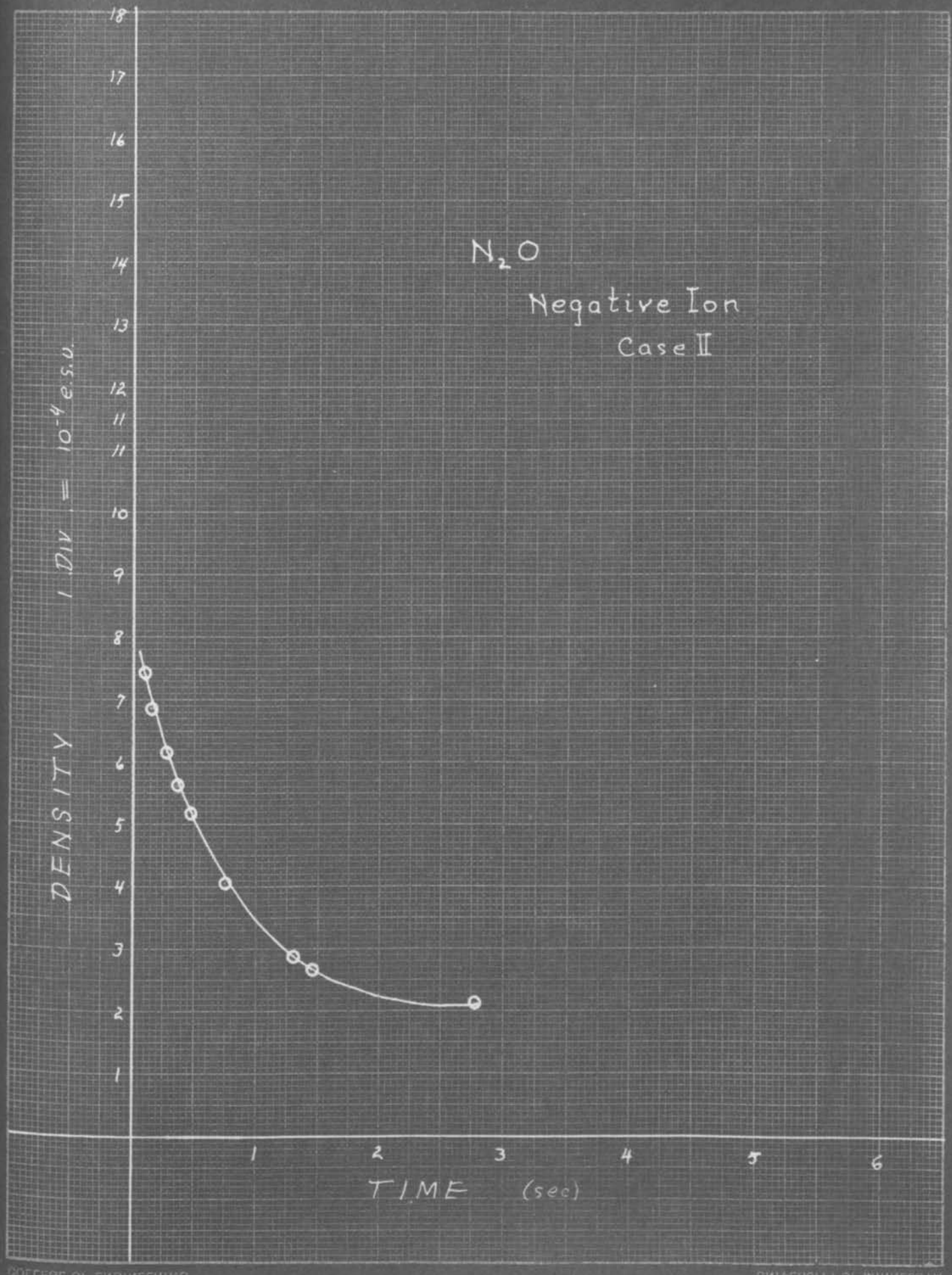



C_2H_2
Negative Ion
Case II
DENSITY 1 Div. = 10^{-4} e.s.u.
TIME (sec.)
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6

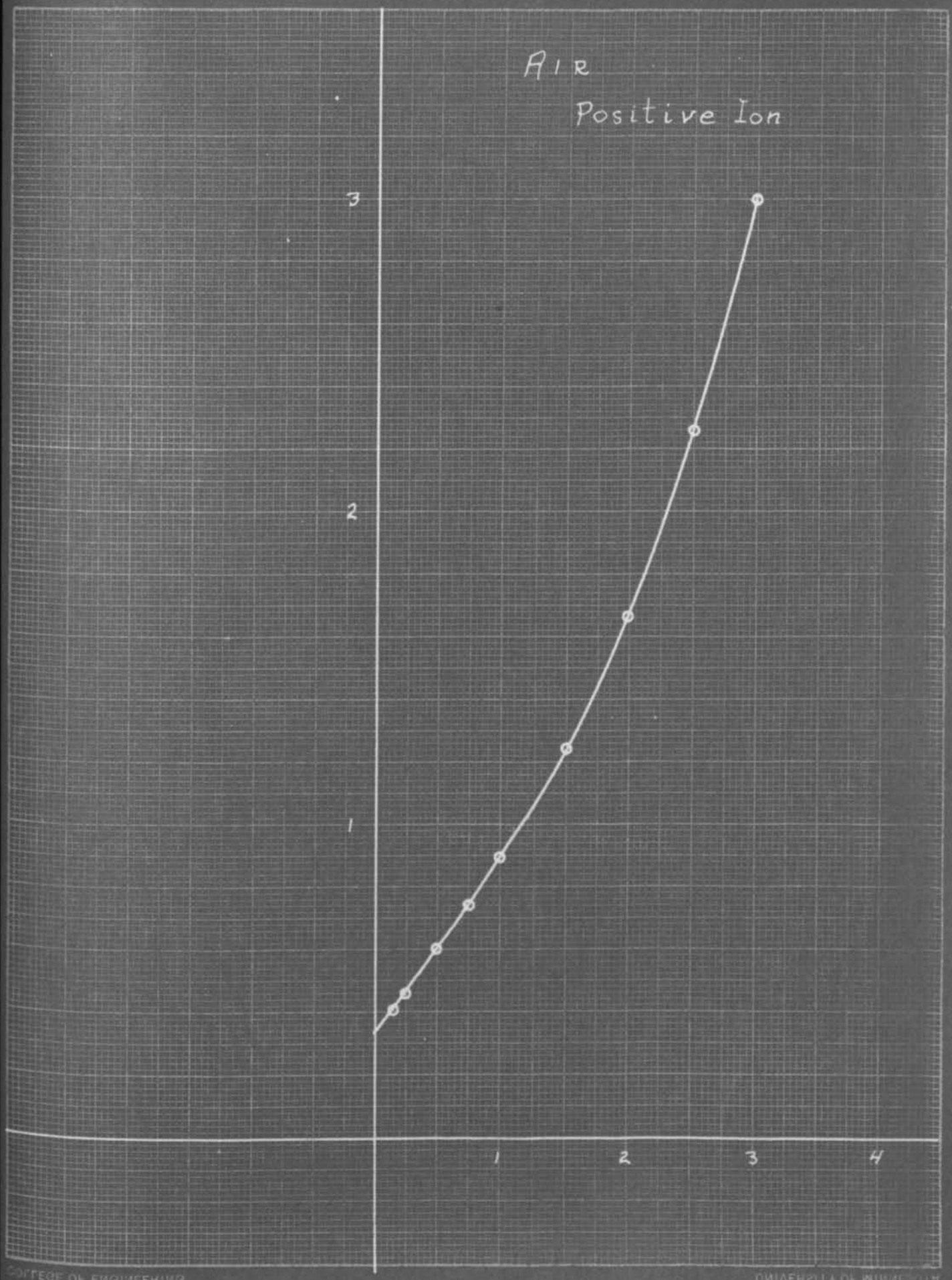

N_2O
Positive Ion
Case I
DENSITY
1 Div. = 10^{-4} e.s.u.
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
TIME (sec.)

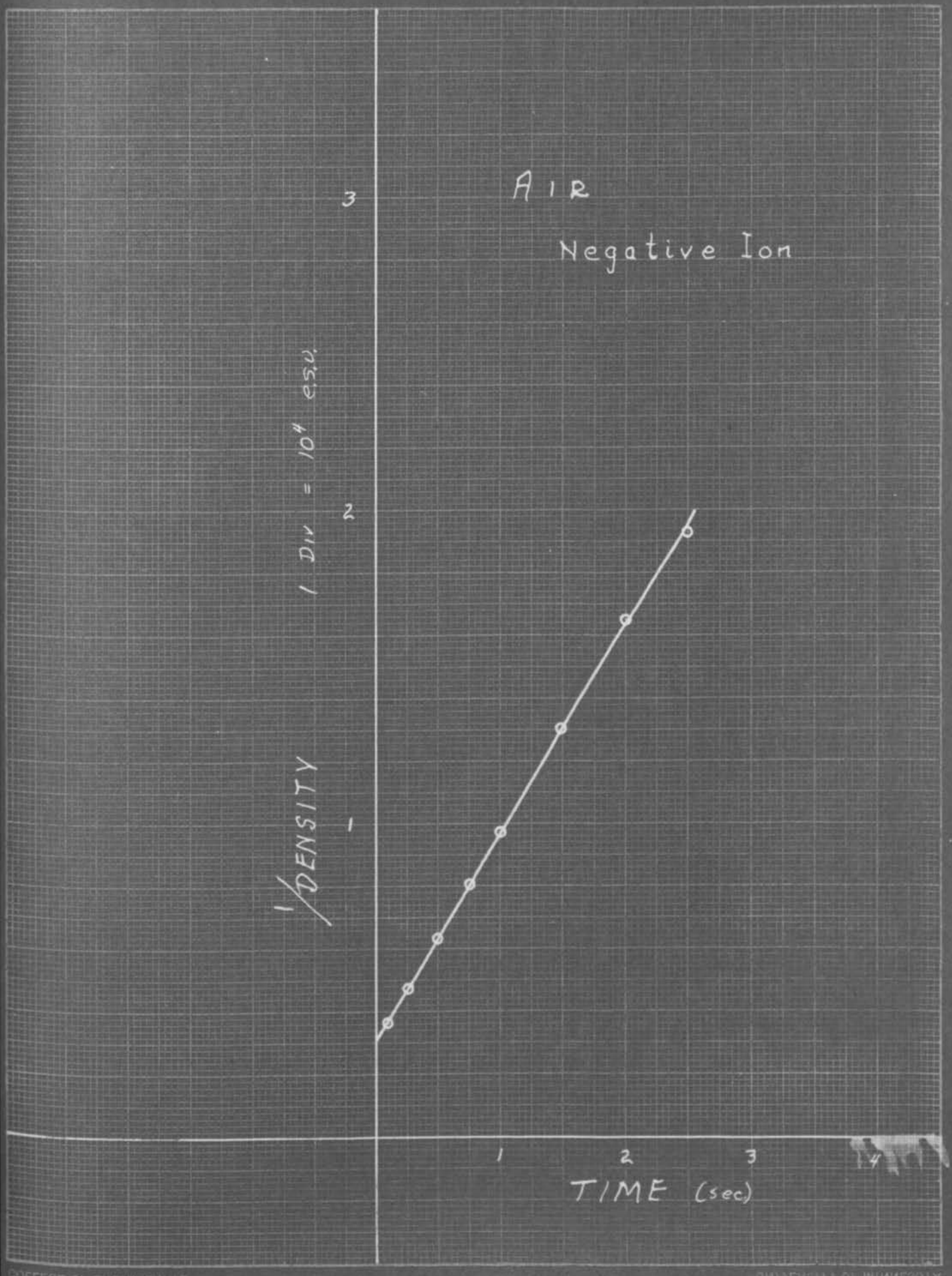

N_2O
Positive Ion
Case II
DENSITY
1. Div. = 10^{-4} e.s.u.
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
TIME (sec.)

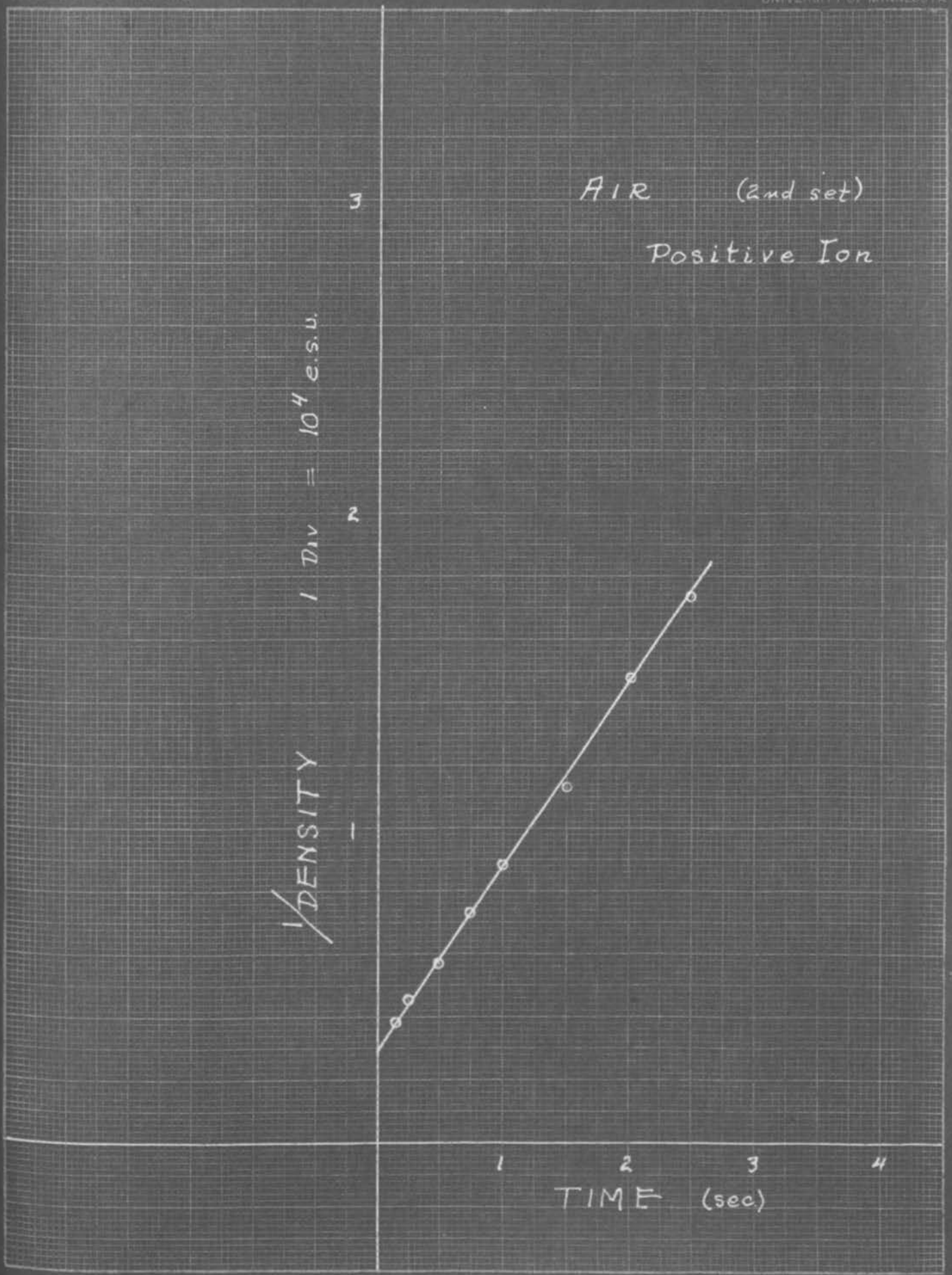


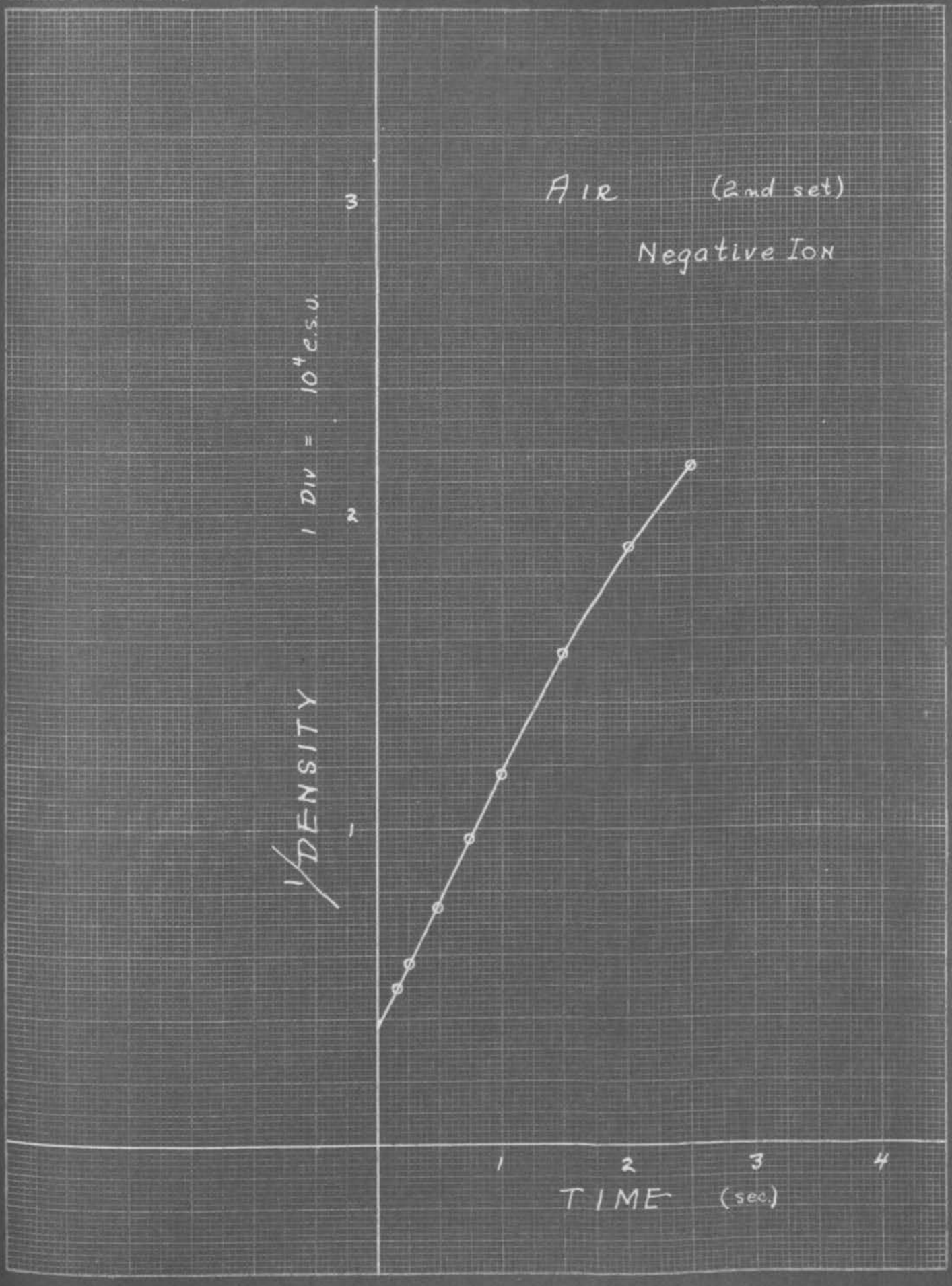


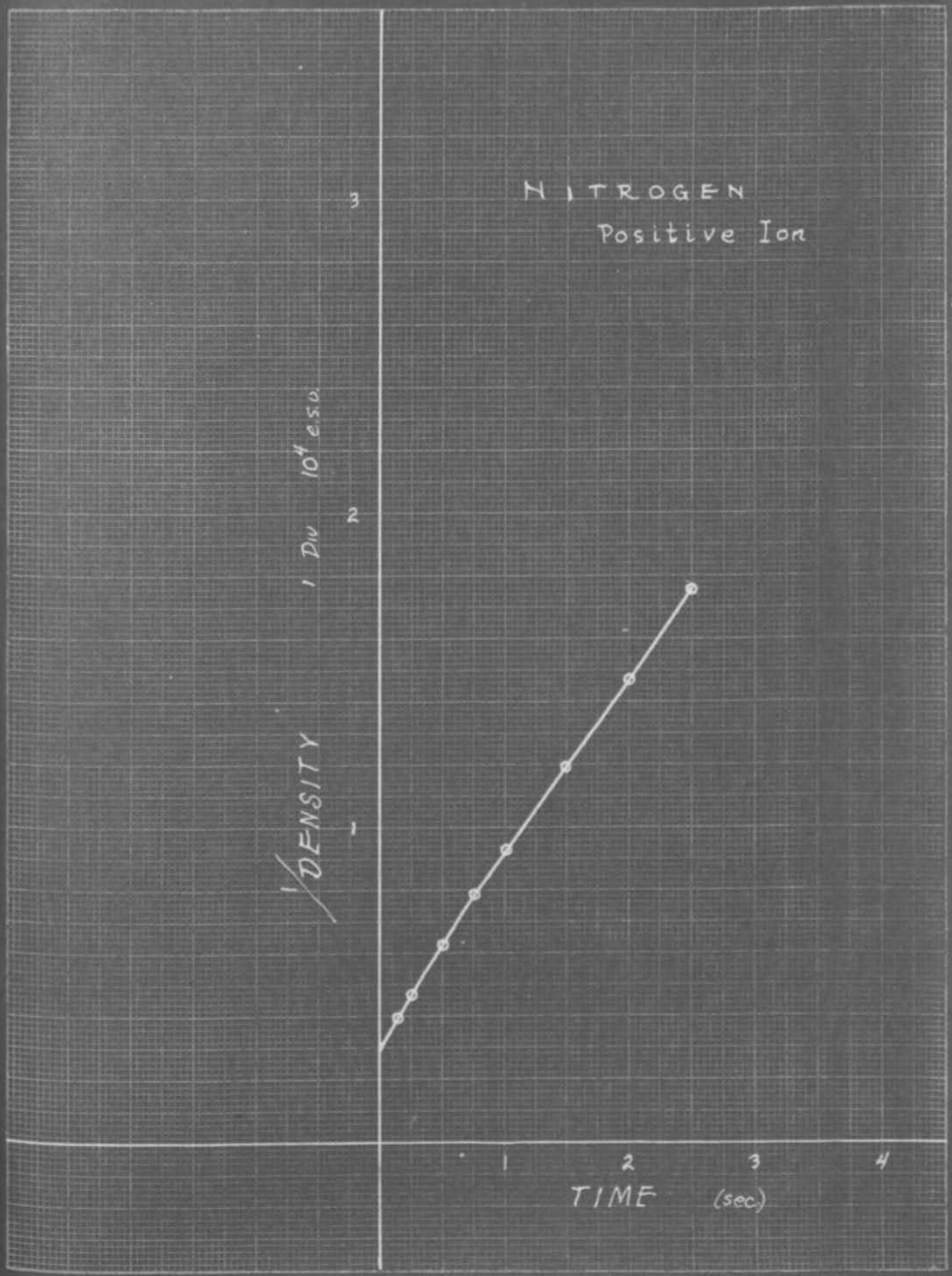
CURVES SHOWING VARIATION OF RECIPROCAL OF CHARGE DENSITY WITH TIME.

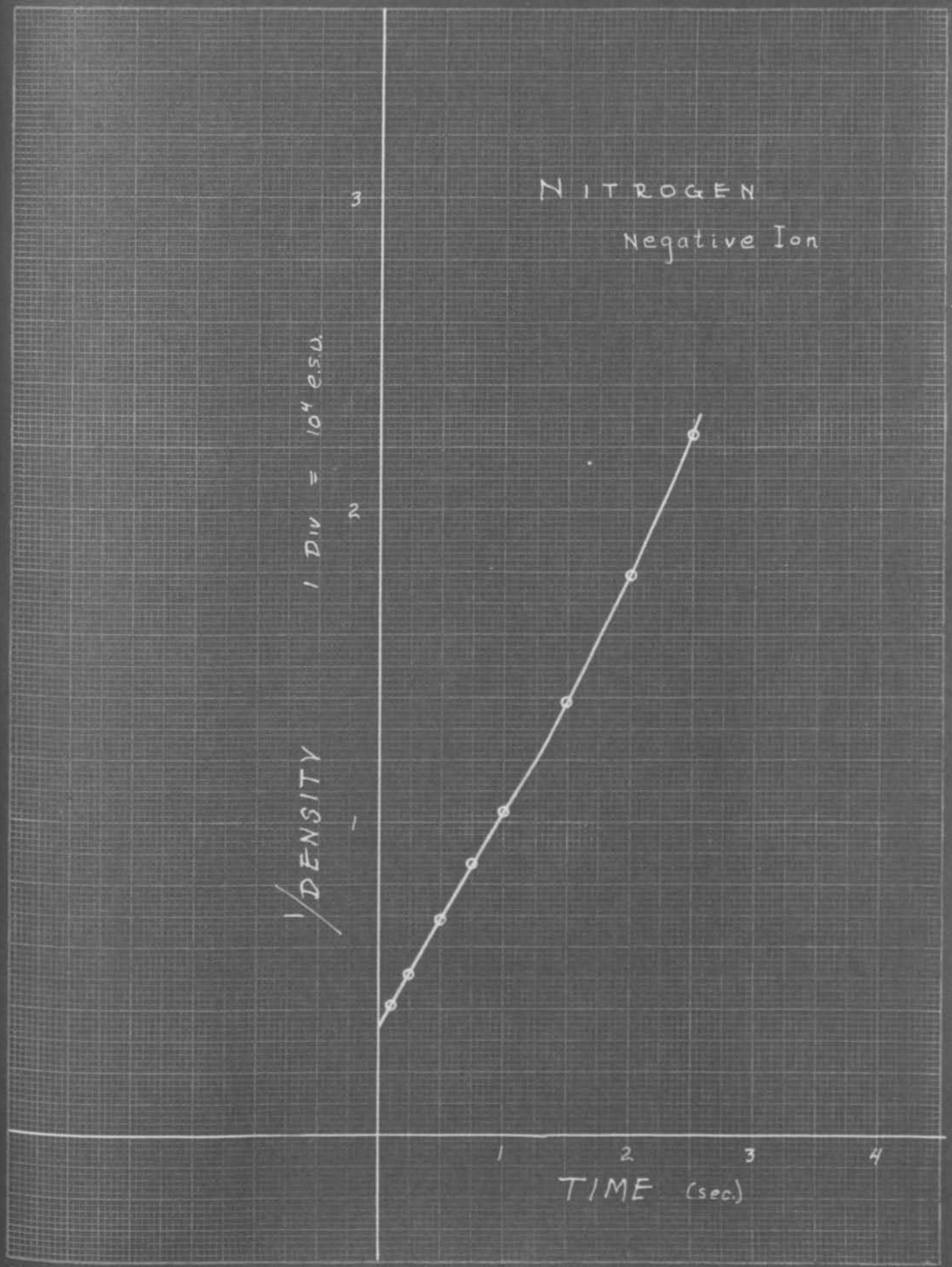

AIR
Positive Ion
3
2
1
1
2
3
4

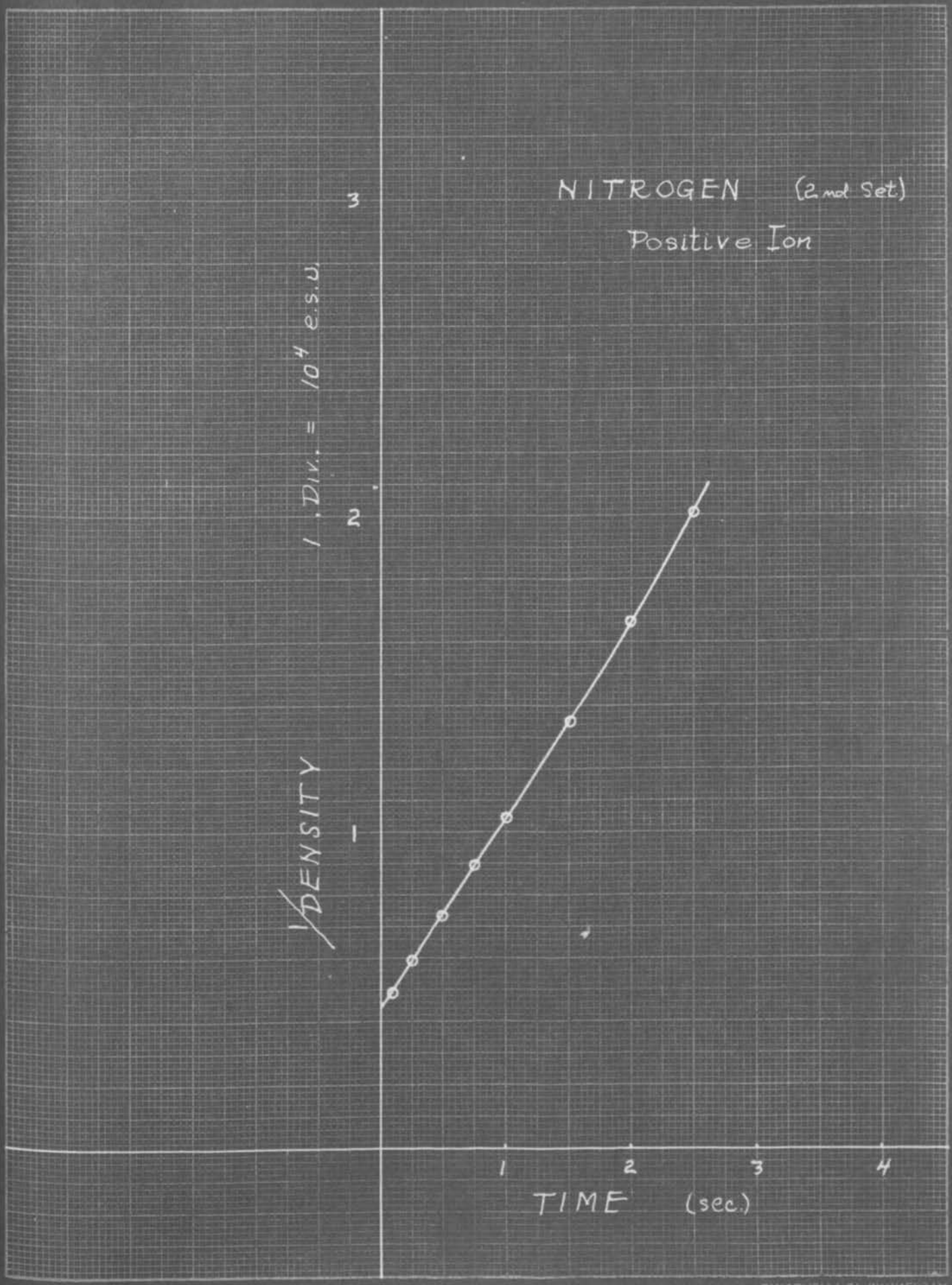


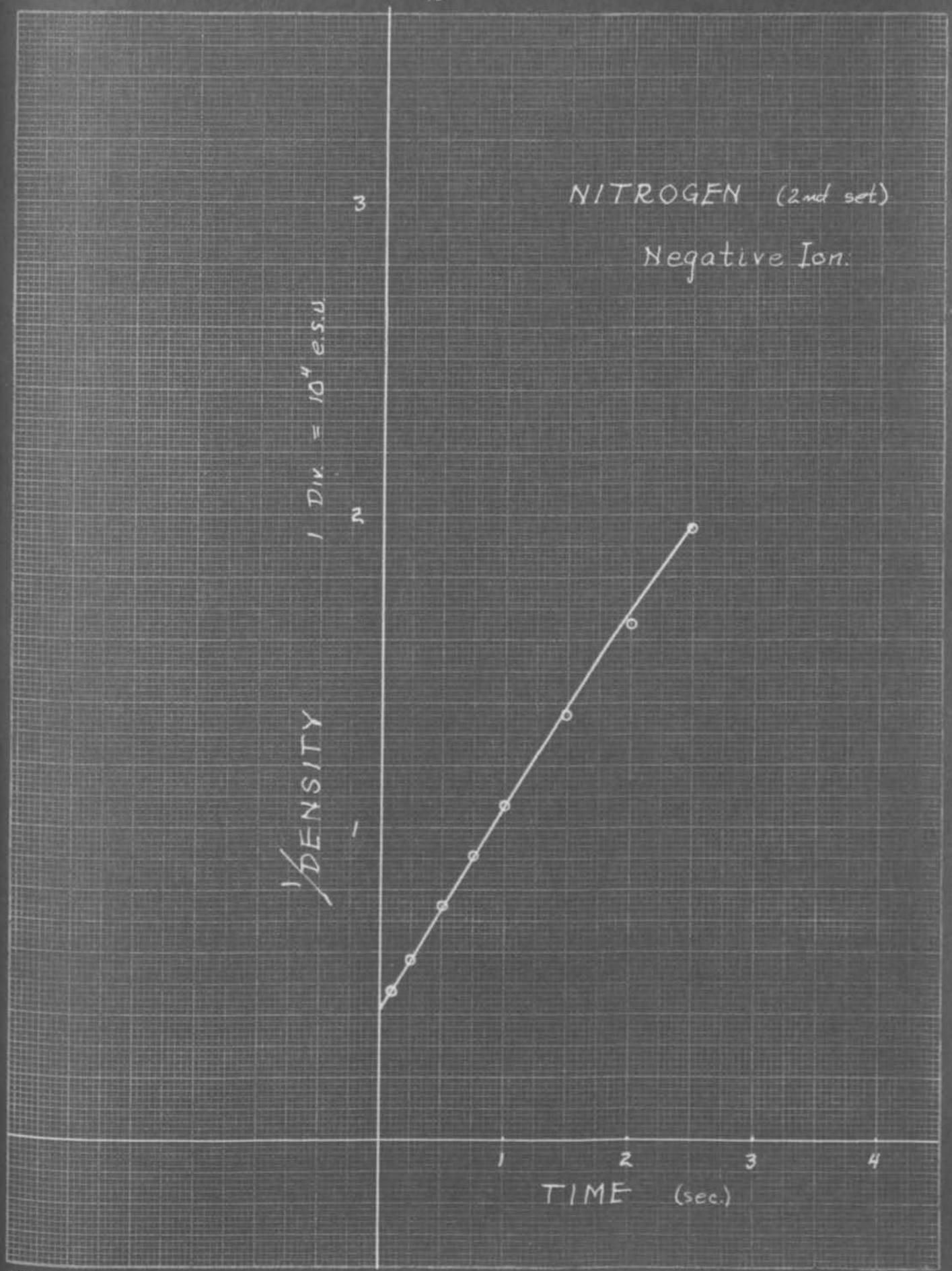

AIR (2nd set)
Positive Ion
1/DENSITY
1 Div = 10^4 e.s.u.
3
2
1
1
2
3
4
TIME (sec)

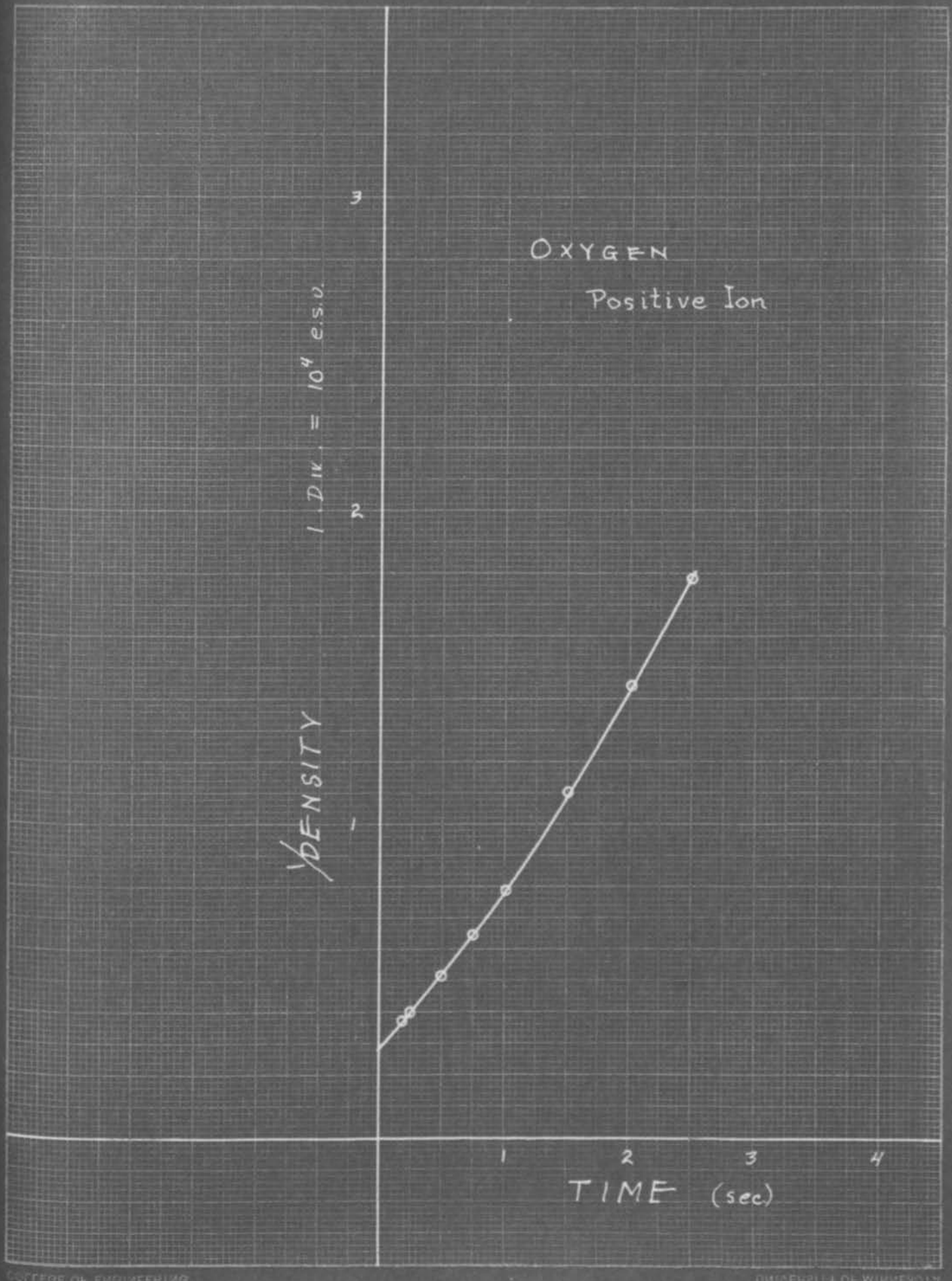

AIR (2nd set)
Negative Ion
1/DENSITY
1 DIV = 10^4 e.s.u.
3
2
1
2
3
4
TIME (sec.)

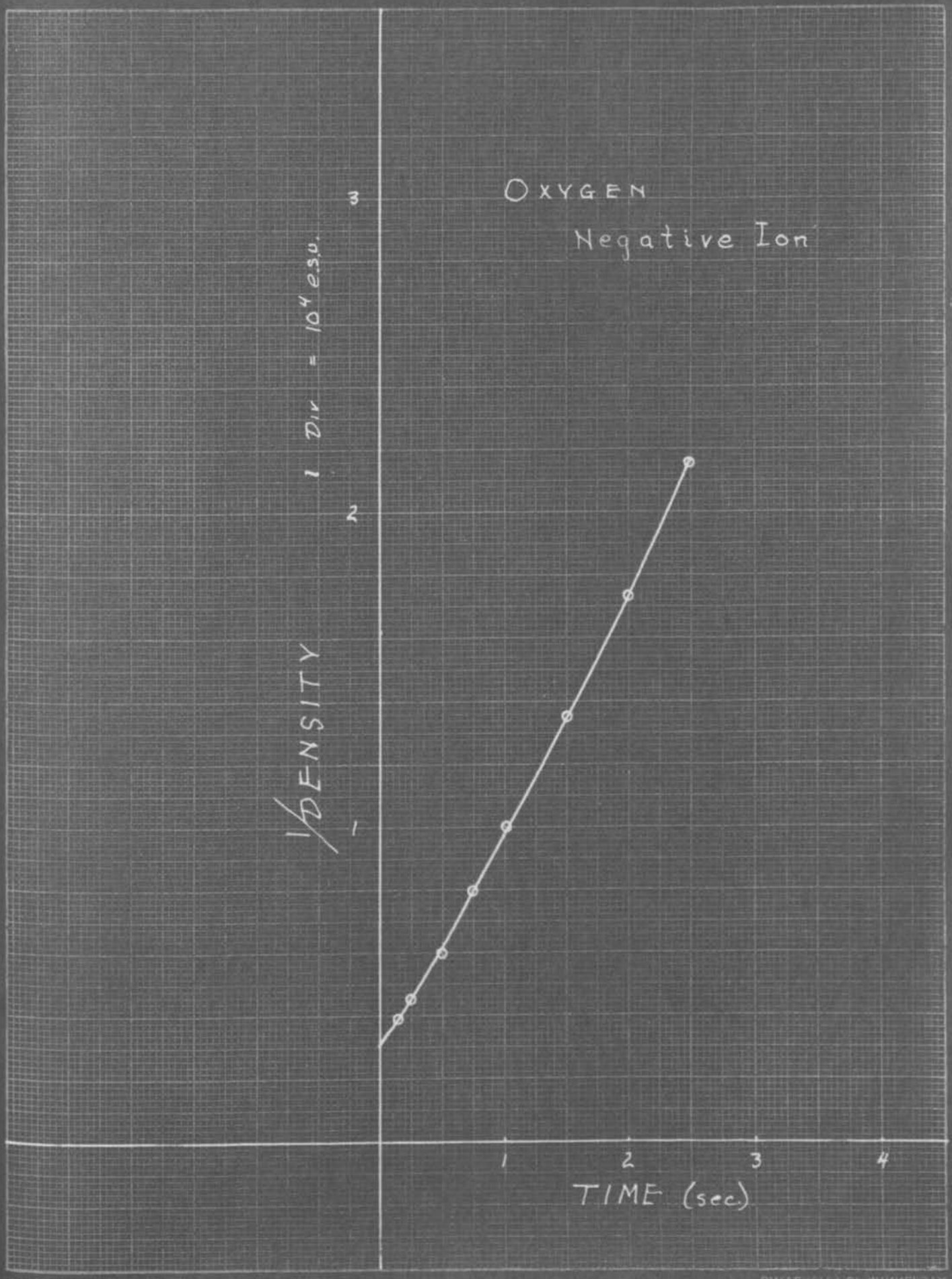


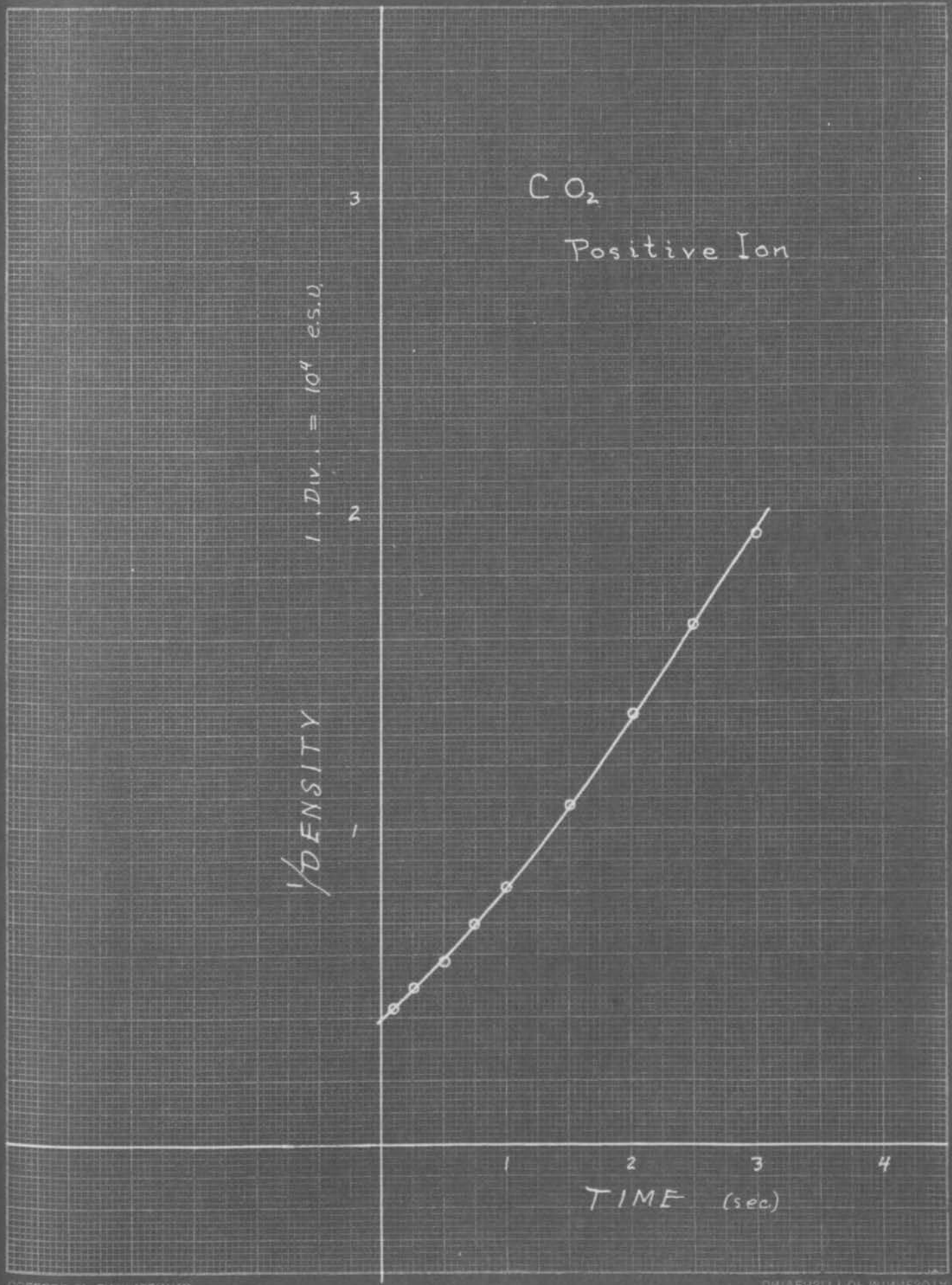


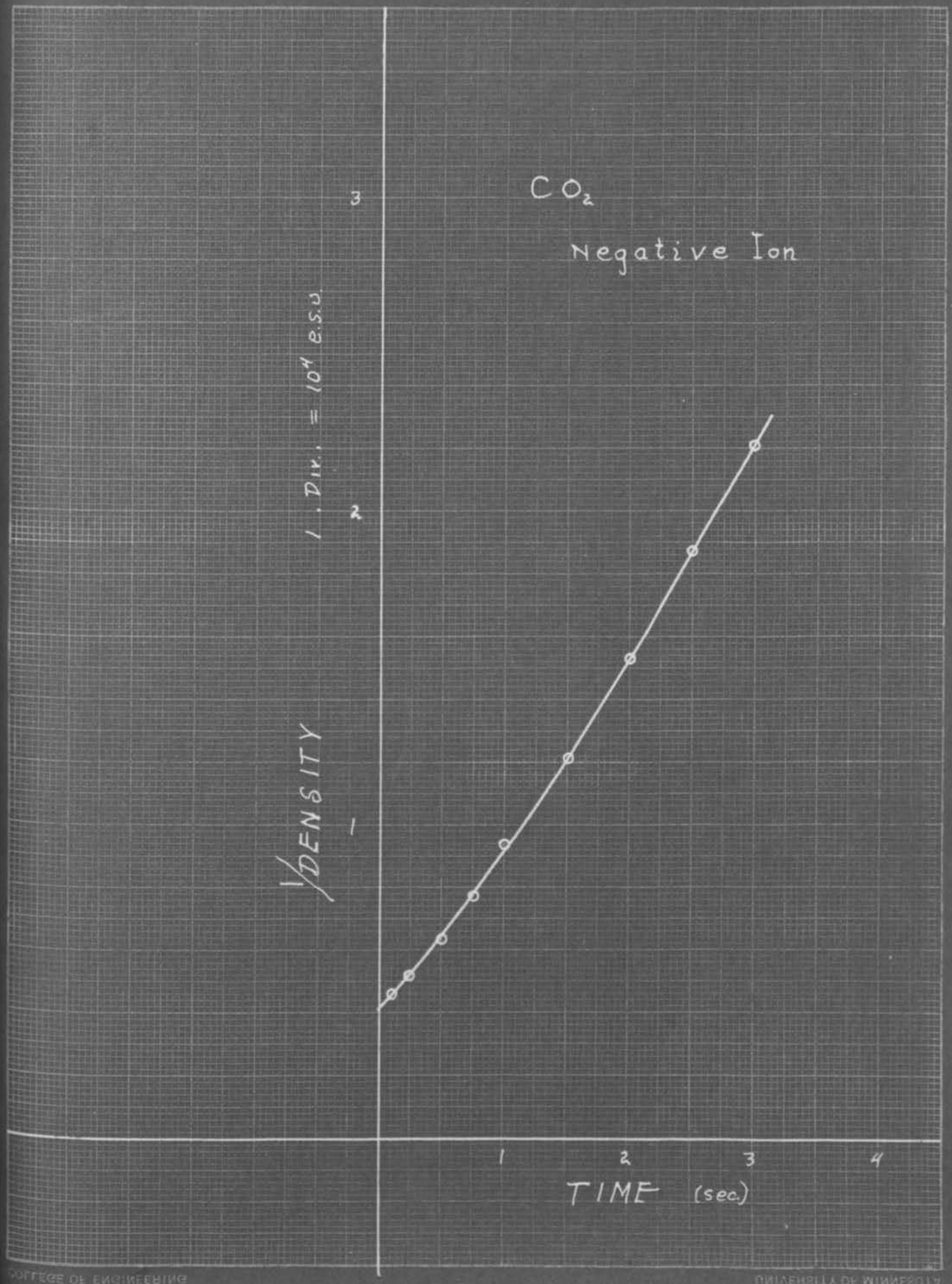


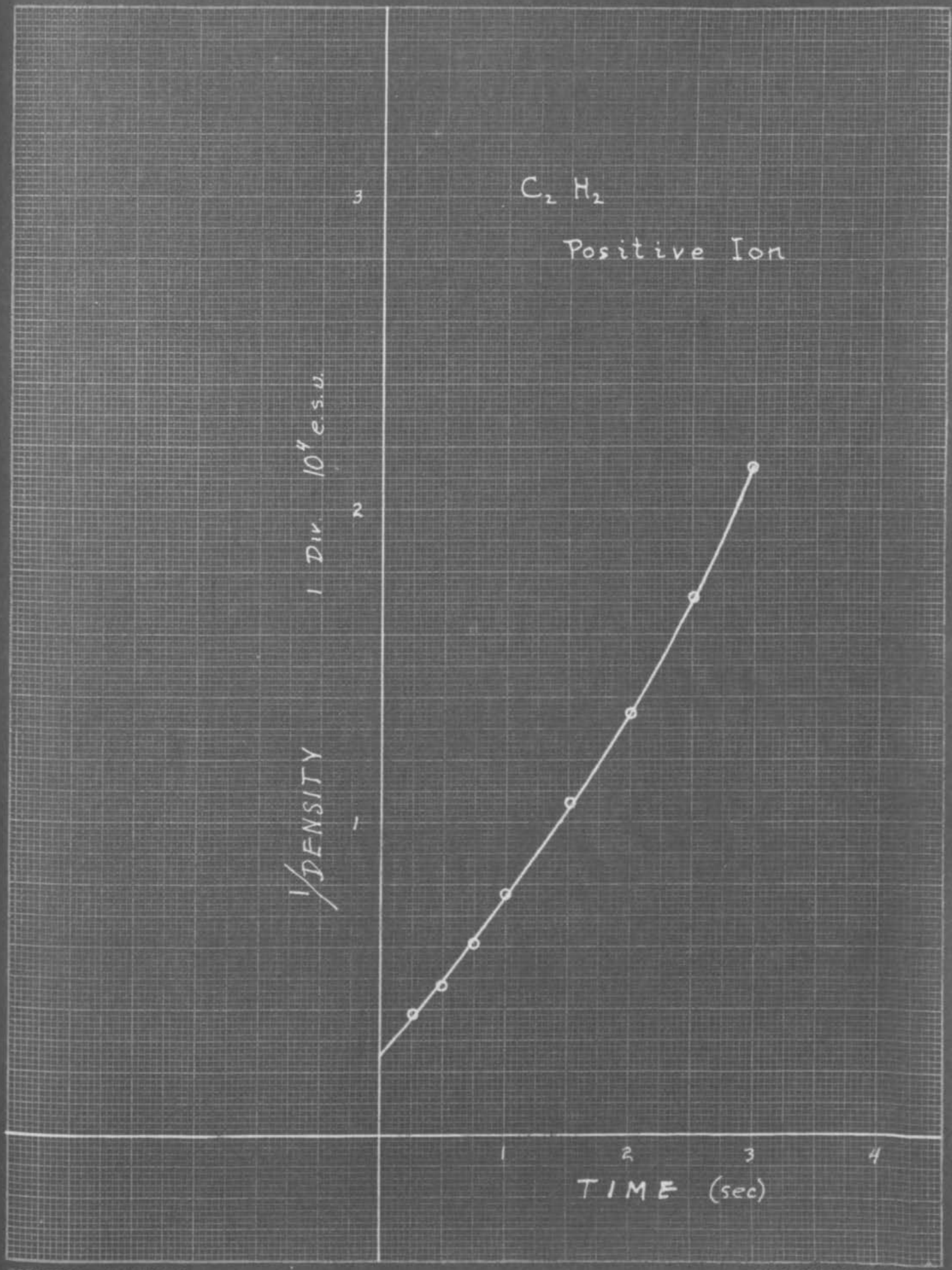


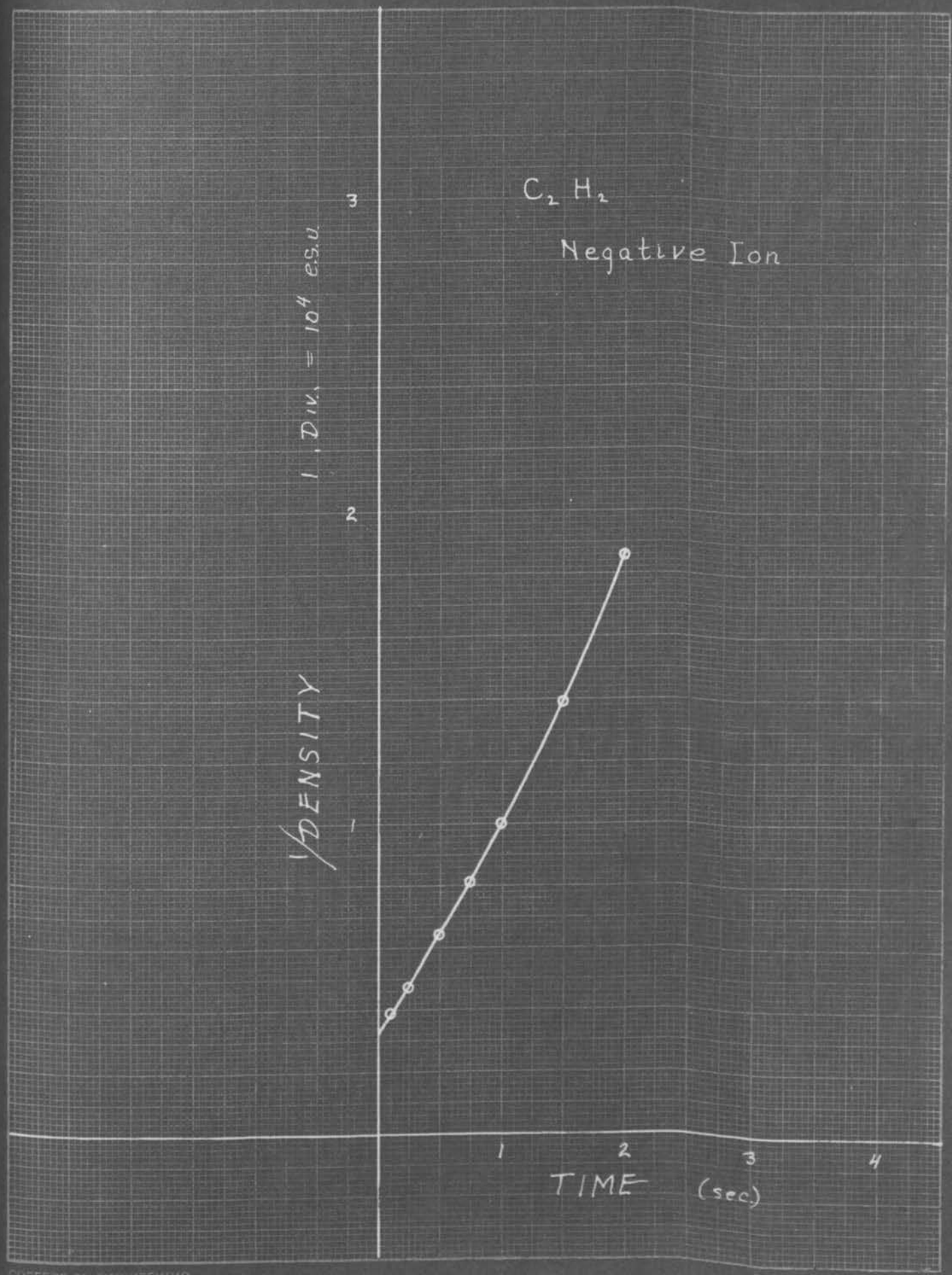


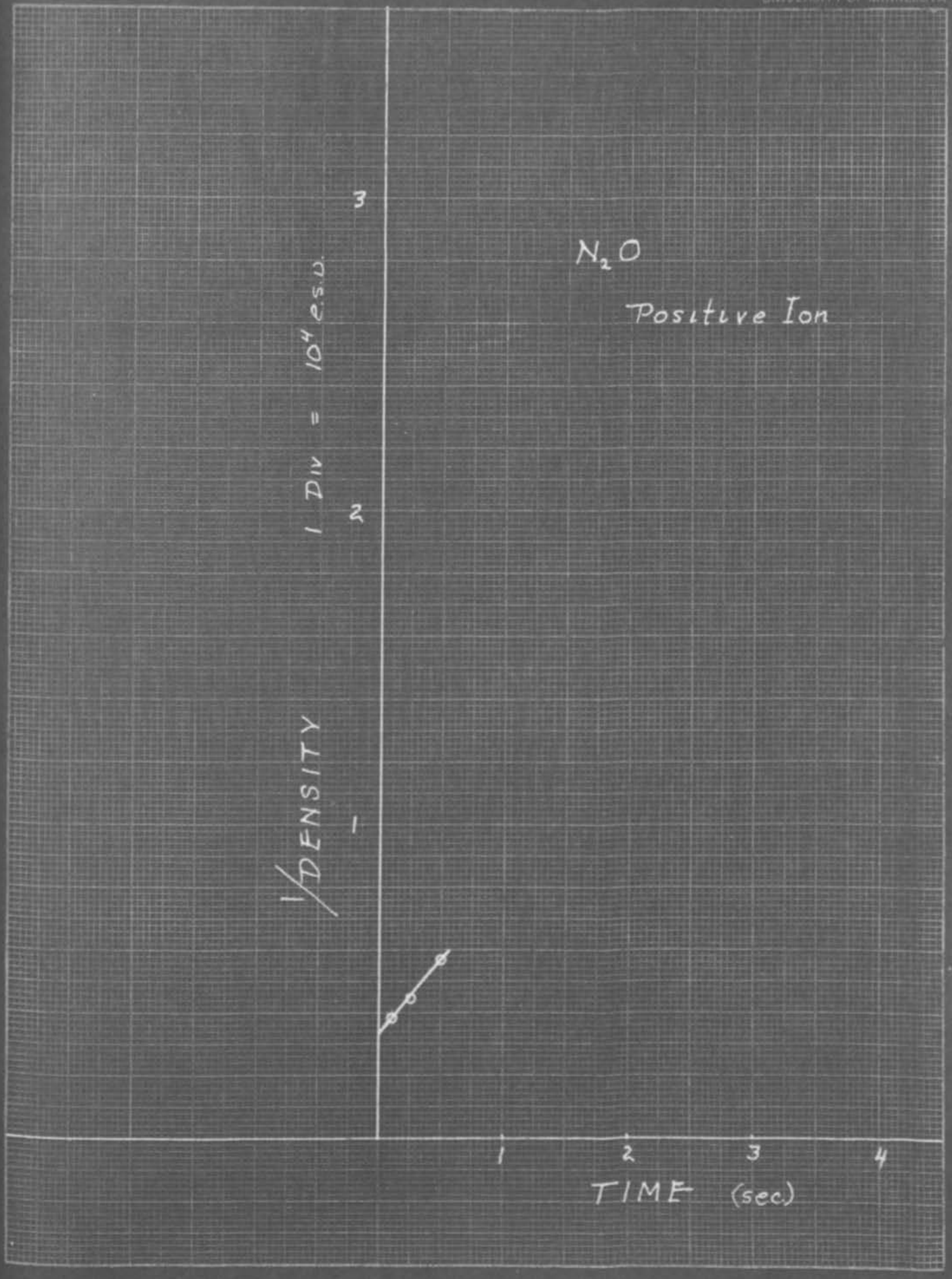


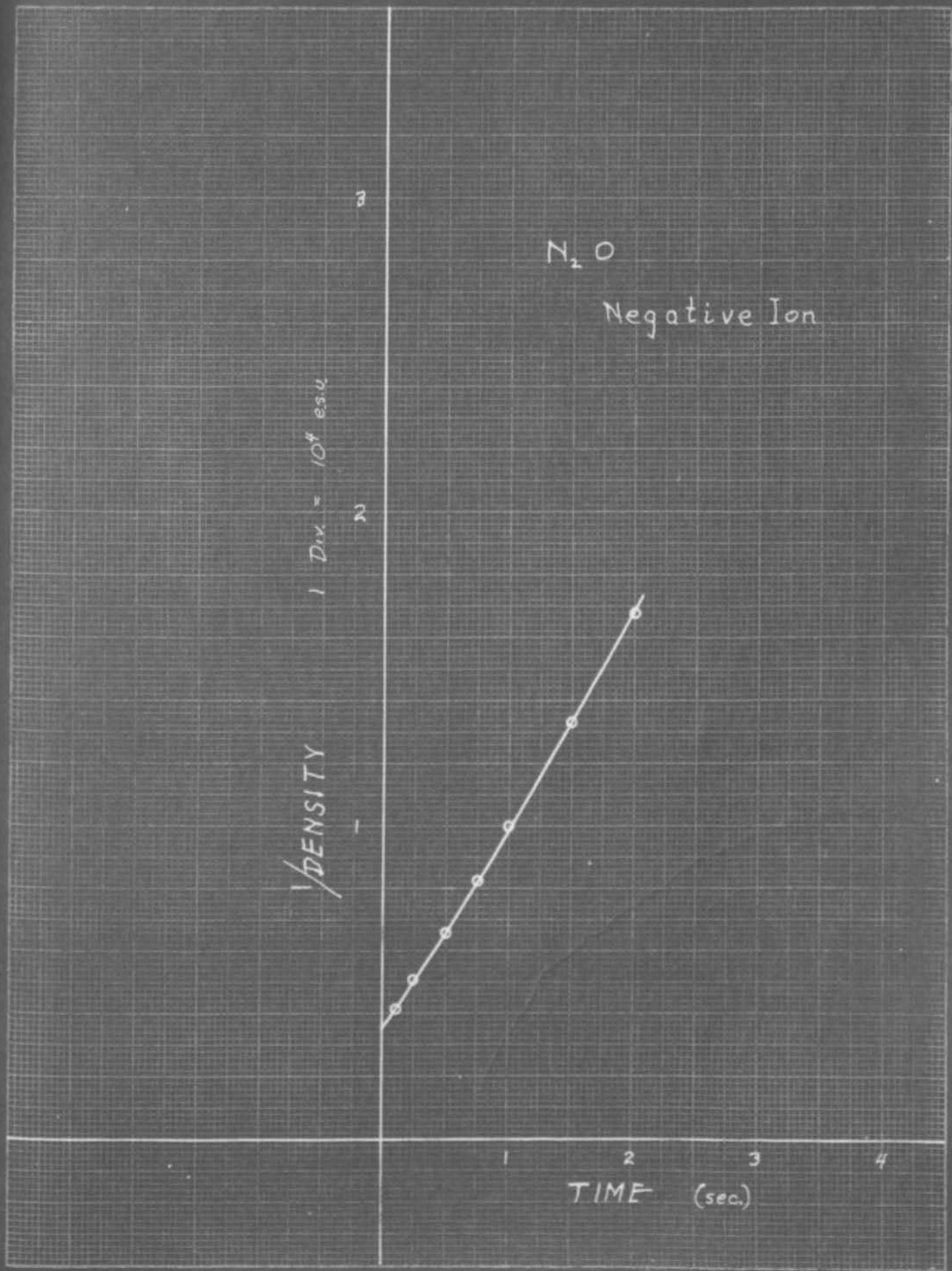









N_2O
Positive Ion
1 Div = 10^4 e.s.u.
1/DENSITY
1
2
3
1
2
3
4
TIME (sec)


N_2O
Negative Ion
1/DENSITY
1 Div. = 10^4 e.s.u.
TIME (sec.)
1
2
3
4

Results.

Sets of readings were obtained for air, nitrogen, oxygen, carbon-dioxide, acetylene, and nitrous oxide. A table of values of mobilities obtained is given below, with a table of previously determined values for the same gases.

	positive ion	negative ion	mobility of neg. ion / mobility of pos. ion
Air	1.55	1.73	1.10
Air (2nd set)	1.53	2.10	
Nitrogen	1.61	1.77	1.09
Nitrogen (2nd set)	1.58	1.72	1.08
Oxygen	1.67	1.87	1.1
Carbon dioxide	1.11	1.36	1.2
Acetylene	1.35	1.74	1.3
Nitrous oxide	1.25	1.75	1.4

Previously determined values.

Air	1.36	1.87	Zeleny
	1.54	1.78	Wellisch
	1.40	1.70	Langevin
Nitrogen	1.30	1.80	Kia-Lok Yen
	1.6		Rutherford
Oxygen	1.36	1.80	Zeleny
	1.30	1.85	Chattock
Carbon dioxide	.83	.92	Chattock
	.76	.81	Zeleny
	.86	.90	Langevin
Nitrous oxide	.82	.90	Wellisch

To the writer's knowledge no results are available on the specific velocity of ions in acetylene.

As indicated by the curves for nitrous oxide, only a partial set of readings were taken for the positive ion for the reason that the readings varied an unusually large amount. This variation may have been due to some chemical action within the ionization chamber. However, the readings plotted in the curves were of

sufficient consistency to warrant their use in at least estimating the mobility.

It may be noted that the ratio of the mobility of the negative ion to the mobility of the positive ion is smaller in the case of the simple gases than in the case of the compound gases.

Accuracy of Results.

Let us consider the various factors which enter into this experiment to make the results uncertain and compare this method with the other methods which are favorably regarded at the present time.

From experience with the behavior of the apparatus, the writer feels confident that the most variable factor influencing the measurement of charge was the natural ionization taking place within the chamber. The charge due to this ionization would sometimes cause the "balance" readings to vary by .03 volt during a set of observations. There is therefore a possible variation of .03 volts in all of the readings. On the larger readings this effect is less than one per cent, since the larger values of charge density correspond to readings in the neighborhood of 2.00 volts and .015/2.00 = .0075. The percentage of error from this source of course becomes large for the low values of the charge density.

c Consider the curves where the reciprocals of the charge density are plotted. The high values of the charge density become the low reciprocals. A variation of one percent is small in these values. The error of .03 volts causes an appreciable error in the

larger values of the reciprocals, in fact it becomes great enough to account for the deviation of the curve from a straight line in these regions, since the error may be additive in Case I and Case II.

The variation in natural ionization also caused the readings necessary for the calibration of the apparatus to vary, but calibrations for identical conditions of the apparatus for different gases were made at intervals of days and sometimes weeks and were found to vary among themselves by not more than two percent. Hence it is probable that the error in any one value does not exceed one percent.

Another possible source of error was in the measurement of time by the chronograph. The maximum error occurred in measurement of short time intervals, and may have been three percent. However, the readings for the short time intervals could be repeated (by means of the contacts on the pendulum) with a variation of not more than one percent, although the chronograph was run at different speeds.

Then we must consider the possible error made in determining the slope of the straight part of the $\frac{1}{\rho}$ t, curves. In a representative case it appears that the possible error from this source does not exceed three percent.

Another factor whose effect must be considered is diffusion. If this effect were large in comparison to the effect of self repulsion at high values of ρ , the $\frac{1}{\rho}$, t curve would not be a straight line. The increase of $\frac{1}{\rho}$ with time would be more rapid than that given by a linear relation. Since this deviation from the straight line is not apparent at low values of $\frac{1}{\rho}$, we conclude that the effect of diffusion is negligible for these values.

In this investigation the entire sets of readings for only air and nitrogen were repeated. The two sets of values for the mobilities of the positive and negative ions in nitrogen agree, and the values for the positive ion in air agree. If one notices the case one and case two curves for the negative ion in air, one will find that the case one curves agree, but in the case two curves, there is a discrepancy. From the behavior of the apparatus during these two sets of readings, it seems certain that the first set of observations is the better. This is also born out by the appearance of the case one and case two curves.

Although these sets of readings have not been repeated for each gas, the determination of one set of readings is the equivalent of several mobility determinations. From the equation $\frac{1}{\rho} - \frac{1}{\rho_0} = 4\pi K t$ it is obvious that only two values of ρ and the corresponding time interval are necessary to determine k. The linearity of the curve shows a close agreement between these various possible determinations of the mobility. It may be noted that it is a point in favor of the self-repulsion method that theoretically the $\frac{1}{\rho}, t$ curves should be straight lines, and that the curves obtained from the experimental data are straight lines in their most accurate portions.

A method whichhas been considered one of the most successful for measuring the mobilities of gaseous ions is the alternating field method. Theoretically the current should have a certain constant value for different plate distances until these distances become greater than a certain critical value when the current should fall immediately to a zero value. On account of diffusion, self-repulsion and the fact that the ions do not start from the same point on the gauze this does not happen. The type of curve actually obtained may

be seen in figure 4 of Loeb's paper[1] and figure 2 of Kia-Lok Yen's paper[2]. The most nearly straight parts of these curves are extended and their intercepts with the x axis are taken as the critical distances. There has been given no accurate theoretical basis for determining the critical distances in this way, however if this method were theoretically correct there would still be uncertainty in determining the slopes of these curves, as the curves referred to above show. That this method leaves something to be desired in the way of consistency may be seen from the different values of mobility which Kia-Lok Yen obtained when he used different voltages. On page 346 of his paper he averages values of mobilities of the positive ion in air of the orders of 1.1 and 1.6, values which differ from each other by over 30%.

While the Zeleny method is theoretically exact, it appears from figure 10 in Blackwoods work[3] which is the most recent work published on the Zeleny method, that some uncertainty would be involved in determining actual mobilities from the experimental curves.

The accuracy of the method which Professor Erikson has recently been using cannot be discussed as the data is not yet available.

1. Loeb, Phys.Rv. V8, p633, 1916.
2. Kia-Lok Yen, Phys.Rv. p337, 1918.
3. Blackwood, Phys.Rv. Aug.1920.

Summary.

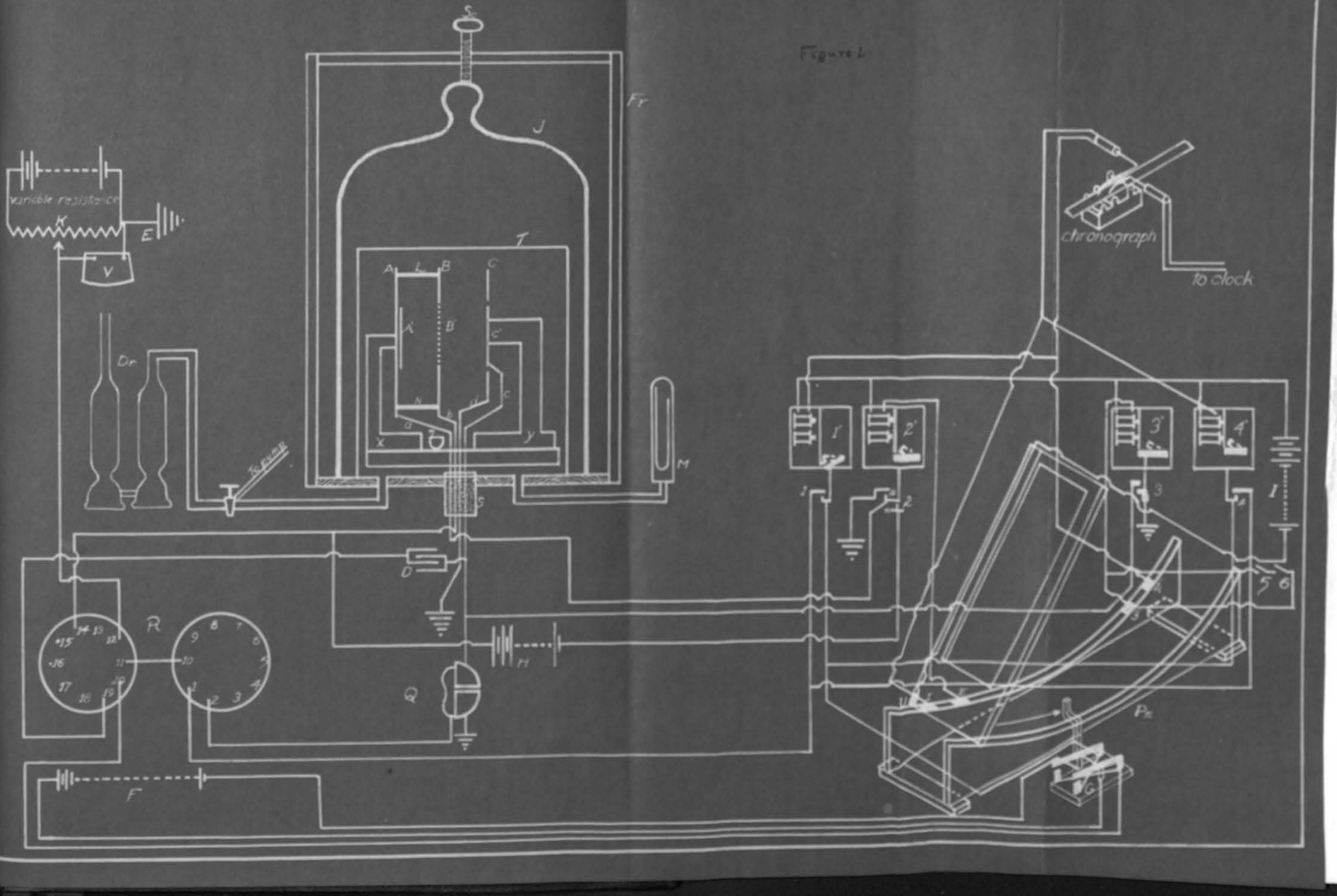
1. The Self-repulsion method is different in its general features from those usually employed for measuring the mobilities of gaseous ions. Owing to the fact that it is desireable to attack a problem in various ways the possibilities of the self-repulsion method have been investigated.

2. By this method the mobilities of the positive and negative ions in air, nitrogen, oxygen, carbon-dioxide, acetylene, and nitrous-oxide have been measured.

3. The Self-Repulsion method compares favorably in accuracy with the best methods for determining ionic mobilities. An outstanding feature of this method is the agreement between experimental results and mathematical theory.

In conclusion the writer wishes to express to Professor Swann under whose direction this investigation was performed, her sincere appreciation and gratitude for his continued interest and assistance in the solution of difficulties.

Figure 1.


variable resistance
K
E
V
Dr
To pump
Sc
J
Fr
T
A
L
B
C
A'
B'
C'
N
a
b
c
x
y
M
S
D
R
Q
H
F
chronograph
to clock
1
1'
2
2'
3
3'
4
4'
5
6
Pe
G